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UTILIZATION OF C_4's AND C_5's OF ETHYLENE PLANTS AND FCC UNITS THROUGH TRANSFORMATION TO OCTANE BOOSTERS FOR UNLEADED GASOLINE

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MICROMEDIA

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CHAPTER ONE

GENERAL

1.0 GENERAL

This is a final report for the Department of Energy, Mines and Resources (EMR), CANMET Division. It is the result of a solicited proposal submitted to EMR in November 1986 - an energy conversion cost-shared program.

The work program was broken down into the following tasks:

- information retrieval;
- processes and technologies;
- catalysts;
- products;
- report writing.

The objective of the project is to acquaint ourselves with:

- state of the art technologies and processes for the processing of C_4's and C_5's to octane enhancers for the gasoline pool;

- the nature and characteristics of the catalysts used in these processes;

- the possible products (and how to obtain the desired product slate);

- how to analyse the feed and products.

1.1 BACKGROUND

Lead in Canadian gasoline is scheduled to be phased out by the end of the century. Table 1.1 gives a summary of the time schedule for the execution of the above.

TABLE 1.1 MAXIMUM ALLOWED LEAD CONTENT (g/l) (Source: 1)

	Leaded Gasoline	Unleaded Gasoline
Until Dec.31/86	0.77	-
From Jan. 1/87 to Dec.31/92	0.29	0.013
After Dec. 1992	0.00	0.000

The above regulations in Canada imply that refiners must find ways of upgrading the octane rating of their gasoline pool. This could be achieved in various ways but one of the less capital intensive is the addition of octane enhancers, generally called oxygenates. The Canadian General Standards Board (CGSB) has defined oxygenated gasoline as a blend of alcohols (up to C_4) and/or ethers with unleaded or leaded gasoline. The maximum content of oxygen in oxgenates added to gasoline is limited to 3.7% by weight while methanol content is limited to 5 vol. %.

The major oxygenated fuels used in gasoline are:

- MTBE (Methyl Tertiary butyl Ether);
- TAME (Tertiary Amyl Methyl Ether);
- TBA (Tertiary Butyl Alcohol);
- MeOH (Methanol);
- EtOH (Ethanol);
- IPA (Isopropanol).

These oxygenates are gaining in popularity for the following reasons:

- their ability to improve the octane rating of gasoline;
- their capability of increasing the overall gasoline pool;
- the fact that hydrocarbon sources which formerly were burned as fuel can now be utilized to give a desired product;
- worldwide restrictions in the lead content of gasoline spearheaded by environmental lobby groups.

All the above have culminated in a process technology race. The runners are technology development groups while the goal is the development of technologies that would take C_4's and C_5's from ethylene plants and FCC Units and convert them to oxygenates (marketable and higher priced products).

There had also been a marked improvement in U.S. gasoline octane ratings since 1985 through the use of oxygenates. The U.S. Environmental Protection Agency (EPA) enacted regulations in March 1985 restricting the lead content in gasoline to 0.50 gram per gallon as of July 1, 1985, and further to 0.10 gram per gallon as of January 1, 1986. The EPA is currently evaluating a total ban and industry sources don't expect the total ban to be effective earlier than 1990. With the free trade agreement between Canada and the United States signed, oxygenates production in Canada looks very favourable.

In the European Economic Community (EEC) countries, the current allowable amount of lead in gasoline ranges from 0.15 gram to 0.40 gram per liter, and all member countries are to reduce the permitted lead content to 0.15 gram per liter by October 1989. West Germany is to ban regular leaded gasoline by February 1988 while Luxembourg will ban it by July 1988.

The Japanese government has also recommended a phasedown on the use of lead anti-knock mixes in gasoline. The Japanese Industrial Standard (JIS), changed in mid 1986, stipulates that the lead content of both regular and premium gasoline should be less than detectable by atomic absorption analysis. This standard is equivalent to a total ban although production of negligible amounts of leaded gasoline will be allowed with special permission from the Ministry of International Trade and Industry (MITI) for testing purposes.

Table 1.2 summarizes the maximum allowable lead content of motor gasoline of the western industrialized countries as of January 1, 1987.

TABLE 1.2 MAXIMUM ALLOWABLE LEAD CONTENT OF MOTOR GASOLINE OF THE WESTERN INDUSTRIALIZED COUNTRIES as of JANUARY 1, 1987 (Source: 1)

	Grams of Lead per Liter of Gasoline Allowable	
Country	Regular Grade	Premium Grade
Austria	0.000	0.150
Belgium	0.400	0.400
Canada	0.29	0.013
Denmark	0.150	0.150
Finland	0.150	0.150
France	0.400	0.400
Greece	0.400	0.400
Ireland	0.400	0.400
Italy	0.400	0.400
Japan	0.000	0.000
Luxembourg	0.400	0.400
Netherlands	0.150	0.400
Norway	0.150	0.150
Portugal	0.400	0.635
Spain	0.400	0.600
Sweden	0.150	0.150
Switzerland	0.150	0.150
United Kingdom	0.150	0.150
U.S.A.	0.0264	0.0264
West Germany	0.150	0.150

1.2 OXYGENATES AND THEIR PROPERTIES

"Oxygenates" is a general term used to describe additives which are octane enchancers to gasoline. These gasoline blending agents which, because they contain oxygen, are referred to as oxygenates. When added to gasoline, the resulting blend is commonly called "oxygenated fuel" or "oxygenated gasoline". The oxygenates of interest as fuel additives worldwide include alcohols - Methanol (MeOH), Ethanol (EtOH), Isopropyl Alcohol (IPA), Isobutyl Alcohol (IBA), Tertiary-Butyl Alcohol (TBA), and ethers - Methyl-Tertiary-Butyl-Ether (MTBE) and Tertiary-Amyl-Methyl-Ether (TAME).

1.2.1 Methanol (MeOH)

Methanol is manufactured in North America almost exclusively from natural gas (2) although it could be manufactured from coal or wood. In Canada three world scale plants produce MeOH - see Table 1.2.1.1.

TABLE 1.2.1.1 METHANOL PRODUCTION IN CANADA
(Source: 3 and 4)

Company	Location	Capacity (Tonnes/yr)
Alberta Gas Chemicals Ltd.	Medicine Hat, Alberta	725,000 (3)
Celanese Canada Ltd.	Edmonton, Alberta	714,000 (3)
Ocelot Industries Ltd.	Kitimat, British Columbia	414,000 (4)

The price of MeOH has fluctuated within the past few years - in January 1987 the market price of MeOH was US $0.21/gallon and in January 1988 it has gone up to US $0.51/gallon and at February 1st, 1988 it is at a price of US $0.53/gallon. (US Gulf Coast price). Economic projections on which plant construction in Canada were based pointed at the price of MeOH being in the range of US $1.25/gallon by 1990 (4).

Table 1.2.1.2 shows North American Methanol producers while Table 1.2.1.3 shows new methanol plants in other parts of the world. A world surplus is predicted but if large quantities are to be used for octane enhancement then demand is expected to catch up with supply by 1990.

TABLE 1.2.1.2 NORTH AMERICAN METHANOL PRODUCERS
(Source: 5)

Producer	Location	Nameplate Capacity (MM US gal/yr)	Process	Feedstock
U.S.A.:				
Arco	Channelview, TX	200	ICI	N.G.
Air Products	Pace, FL	65	ICI	N.G.
Borden	Giesmar, LA	200	ICI	N.G.
Celanese	Bishop, TX	180	Lurgi	N.G.
Celanese	Clearlake, TX	-	ICI	-
Du Pont	Beaumont, TX	250	Lurgi	N.G.
Du Pont	La Port, TX	200	Lurgi	Fuel UV
G.P.	Plaquemine, LA	100	ICI	N.G.
Getty	Delaware City, DE	100	Lurgi	Ref.Gas
IMC/Ashland	Plaquemine, LA	-	Lurgi	N.G.
Monsanto	Texas City, TX	100	ICI	N.G.
Tenneco	Pasadena, TX	-	Lurgi	N.G.
Tenn-Eastman	Kingsport, TN	50	Lurgi	Coal
CANADA:				
Alberta Gas Chemical	Medicine Hat, Alta.	260	ICI	N.G.
Celanese	Edmonton, Alta.	200	ICI	N.G.
Ocelot	Kitimat, B.C.	130	ICI	N.G.
MEXICO:				
Pemex	San Martin	60	Lurgi	N.G.

TABLE 1.2.1.3 NEW METHANOL PLANTS
(Source: 5)

On Stream	Country	Capacity (MM US gal/yr)	Company
1985	Bahrain	100	Gulf Petrochemical
	E. Germany	200	Industrie Analgen
	Libya	100	State
	Malaysia	200	Sabah
	New Zealand	500	Petralgas (for gasoline)
	U.S.S.R	330	State
1986	Burma	50	-
	India	20	-
	Indonesia	110	-
	Yugoslavia	66	MSK
1987 - 1988	NIL	NIL	NIL
1988 - 1990	Argentina	200	Petroquimica Austral
	Argentina	50	Recinfor
	Chile	200	Signal Group
	Sharjah	167	-
	Trinidad	100	NEC

Technically, MeOH or EtOH could be used directly to fuel automobiles or blended with gasoline provided suitable modifications were made to:

- the fuel composition;
- the fuel distribution system in the vehicle;
- the vehicles themselves.

However, startability in cool and cold weather would remain a problem with straight MeOH. Other problems envisaged with the use of straight MeOH automative fuel include (2):

- hazards associated with MeOH toxicity;
- vapour explosibility of MeOH;
- dramatic increase in volumetric fuel consumption (about 60%) when compared to gasoline which would require very large vehicle tanks, more storage and transporation capacity, e.g. bulk tanks, pipelines, pumps, tank trucks, etc.;
- replacement of polyester-bonded fiberglass used for service station tanks and lining bulk tanks with a methanol resistant material;
- transition from a gasoline to a methanol fueled automobile population.

Gasoline blended with MeOH alone is unsatisfactory because the presence of water will cause phase separation - separation into distinct layers or phases. Methanol has a strong affinity for water. To prevent this separation, the fuel must be as dry as possible and other alcohols (normally higher alcohols of longer chain length) must be added to stabilize the blend. These higher alcohols used to stabilize the blend and prevent phase separation are known as cosolvents. EtOH, IPA, IBA and TBA may be used as cosolvents; typically however, TBA is the most common cosolvent used. A few problems associated with MeOH - gasoline blends other than phase separation in the presence of small amounts of water include:

- vapour lock;
- loss of driveability;
- increased evaporative emissions;
- incompability with some fuel system materials;
- reduced fuel economy (typically 5% for a 10% blend) in line with a decrease in heat or combustion.

1.2.2 Ethanol (EtOH)

Ethanol is produced worldwide either from a fermentation/distillation process (from grain) or from synthetic processes (from ethane or ethylene).

Ethanol can be added to gasoline as a cosolvent to MeOH or blended with gasoline on its own as a product known as "gasohol".

Production of EtOH in Canada is limited to a few companies as shown in Table 1.2.2.1. Production in the USA is also included in the table. Incentives have supported the growth in the use of agricultural based Ethanol both in Canada and the USA. In the United States, the incentives started with the National Energy Act of 1978 which provided US $.04/gal Federal Tax break for EtOH in gasoline which has increased to US $.06 in recent years. There are also various state tax incentives for gasohol ranging from US $.01 to US $.16/gal. All federal and state exemptions are scheduled to expire in 1992.

TABLE 1.2.2.1 Major Ethanol Producers in Canada and the USA
(Source: 1 and 6)

Company	Location	Capacity (MM US gal/yr)	Process*	End Use
U.S.A.				
Archer Daniels	Midland CO	240	F/D	Motor Fuel +
Texas Eastman Co.	Longview, TX	26	E	EtOH Derivatives
George Pacific Corp.	Bellingham, WA	5	F/D	Motor Fuel +
Grain Processing Corp.	Iowa	40	F/D	Beverage
Midwest Solvents Co.	Atchison, KS	40	F/D	Beverage/ Motor Fuel
A.E. Staley Mfg.	Decatur, IL	40	F/D	Motor Fuel
South Point Ethanol	South Point, OH	60	F/D	Motor Fuel
Kentucky Agr. Energy Corp.	Franklin, KY	20	F/D	Motor Fuel +
American Syn-Fuels	Federalsburg, MD	8	F/D	Motor Fuel +
Pekin Energy Co.	Pekin, IL	60	F/D	Motor Fuel +
Clinton Corn Proc. Co.	Clilnton, IA	8	F/D	Beverage
Union Carbide Corp.	Brownsville, TX	12	N-Butane Oxide	Ethyl Acetate
Union Carbide Corp.	Texas City, TX	120	E	Derivatives
CANADA		(m^3/day)		
Commercial Alcohols Ltd.	Varennes, Que.	225	E	Motor Fuel +
Mohawk Oil Ltd.	Minnedosa, Man.	25	F/D	Motor Fuel

* Process: F/D = Fermentation/Distillation process
E = Synthetic process (ethane or ethylene based)

Ethanol's price is high relative to other blending agents and is attractive only when governments subsidize it.

Both Japan and Western Europe do not presently use EtOH in gasoline because of the economics.

1.2.3 Tertiary-butyl Alcohol (TBA)

TBA is produced commercially from two major process routes:

a) ARCO Chemical Company Process: This is a two-step method which involves:

   i) reacting isobutane and molecular oxygen at 130-140°C (liquid phase reaction) to produce t-butyl hydroperoxide with tert-butyl alcohol as a major coproduct which is separated from the hydroperoxide;

   ii) The separated t-butyl hydroperoxide is then reacted with propylene (oxidation step at 110°C with a molybidenum catalyst) to produce TBA and propylene oxide. ARCO's process produces 3 lbs. of TBA per lb. of propylene oxide.

b) Shell Chemical Company Process: This process applies the hydration of isobutylene to produce high purity TBA mainly for chemical use.

ARCO is the world's major manufacturer of TBA with a 25,000 BBL/day (380 MM gal/yr) plant at Bayport, Texas and a 10,000 BBL/day plant in the Netherlands.

There is no TBA production in Canada. TBA is, however, the most common cosolvent for Methanol.

Neither TBA nor MeOH is very satisfactory as a blending agent but when used together their individual shortcomings seem to be overcome. This mixture is offered commercially for sale as "Oxinol". Inhibitors are included in order to prevent corrosion.

1.2.4 Other Oxygenates Used as Cosolvents

a) ISOPROPANOL (IPA)
The manufacture of IPA is based upon the hydration of propylene. The only plant in Canada belongs to Shell Chemical, Sarnia with a production capacity of only 312 m^3/day.

b) ISOBUTANOL (IBA)
IBA was produced in Canada by BASF Canad Inc., Montreal but this manufacturing facility has been permanently shut down (100 M^3/day).

1.2.5 MTBE and TAME

Production of MTBE and TAME worldwide is dealt with in detail in Chapter 3. There are presently no manufacturing facilities in Canada. A $270 MM MTBE plant is planned for construction at Clover Bar near Edmonton, Alberta. Production capacity is 500 MM tons/yr (11,000 BBL/day). Partners in the project include Neste Oy, 50%; Celanese Canada Inc. and Hoechst Celanese Corp., 30%, and Trans Mountain Pipeline Co., 20%. Feed would be 26 MM cfd of gas, 640,000 cu. m. of field butanes upgraded to isobutylene and 180,000 metric ton/yr of MeOH (7)

1.2.6 Properties of Oxygenates

The physical properties of oxygenates, especially the alcohols, differ from those of gasoline. This leads to a change in gasoline quality when oxygenates are blended with it.

Table 1.2.6.1 shows the physical properites of oxygenates in comparison to those of gasoline.

The effects of the physical properties on gasoline quality are summarized as follows:

- even when the Reid Vapour Pressures (RVP's) of pure alcohols are lower than those of gasoline, small additions of all the alcohols increase the RVP of gasoline substantially. Subsequent additions have little or no effect on the RVP. Pigatt reports that the effect of Methanol is more marked than that of the other alcohols by a factor of three (1.8).

- MTBE and TAME are less polar than alcohols. The addition of either of them causes no significant increase in gasoline RVP.

- The heats of combustion of the alcohols increase with molecular weight. Those of the ethers are higher than those of the alcohols. All are lower than the value for gasoline.

- The heats of vaporization of the alcohols decrease as their boiling points increase. However, they have much higher heats of vaporization than ether or gasoline.

- The lower alcohols have limits of flammability that make them potentially more hazardous than gasoline.

- The specific gravity of the alcohols are higher than that of gasoline while the ethers have specific gravities similar to that of gasoline.

- The alcohols have an infinite capability to absorb or dissolve water. The solubility of water in the ethers is much less, but several times higher than in gasoline. A gasoline/alcohol blend is therefore prone to phase separation due to small amounts of water. This will lead to increased corrosion of the total tankage and distribution system. In Canada where very cold climate is common, icing in the carburetor or gasoline lines could occur.

- The presence of alcohols significantly deforms the distillation curve while MTBE has no significant effect.

- The increase in Reid Vapour Pressure* and volatility when alcohols are added to gasoline, will make it difficult for refiners to meet specification. This could also cause vapour locking problems.

- Alcohols are good for front end octane number but bad for sensitivity. On adding alcohol to gasoline the sensitivity of the gasoline is increased - its MON becomes low for a given RON. Ethers are better for sensitivity than front end octane number.

* Reid Vapour Pressure (RVP) is the vapour pressure of a product determined in a volume of air four times the liquid volume at 100°F. RVP is an indication of the vapour lock tendency of a motor gasoline, as well as explosion and evaporation hazards. The test is carried out according to ASTM D-323.

TABLE 1.2.6.1 PHYSICAL PROPERTIES OF GASOLINE AND OXYGENATES
(Source: 9, 10, 11)

	MeOH	EtOH	IPA	TBA	SBA(4)	MTBE	TAME	Gasoline
Atmospheric Boiling Point (°C)	64.6	78.5	82.4	82.6	99.5	55.4	86.0	32/210
Density (25/4°C)	0.79	0.79	0.78	0.78	0.80	0.74	0.77	0.72/0.78
Molecular Mass	32.04	46.07	60.09	74.12	74.12	88.15	102.18	
Oxygen Content (wt. %)	50.0	34.7	26.6	21.6	21.6	18.2	15.7	
Heat of Combustion (kJ/kg)	22,707	26,945	33,300	35,590	35,690	38,220		
Heat of Vaporization (kJ/kg)	1,104	839	666	536	562	337		
Flash Point (°C)	6.5	12	13	11	24	-28		-43
Ignition Point (°C)	464	425	456	470	380	460		
Water Solubility at 20°C (wt. %)					36.9	1.3	0.6	200 ppm
Water Azeotrope, atm. b.p. (°C)	none	78.2	80.5	79.9	87.5	52.2		
Water in Azeotrope (wt. %)	-	4.4	12.3	11.8	27.3	3.2		
Reid Vapour Pressure (bars)	0.35	0.16	0.13	0.14		0.61	0.22(2)	0.75
Admixture Limit in Gasoline (vol. %) (1)	5.0	5.0	10.0	7.0	10.0	15.0		
Limits of Flammability % vol. Lower	6.7	4.3	2.0	2.4				1.4
% vol. Higher	36.0	19.0	12.0	8.0				7.6
Actual Octane No. (Research) (5)	114	111	106	113	-	117	112	98
(Motor) (5)	95	94	99	110	-	101	99	88
Typical Blending Values (3) (Research)	130	120	-	108	-	115	111	-
(Motor)	103	106	-	98	-	104	100	-
Effect on Front End Octane Number	good	good	good	fair	-	fair	fair	-
Effect on Sensitivity	poor	poor	fair	fair	-	good	good	-

(1) Erdol Chemie (Methanol with compulsory cosolvent (60/40%)
(2) Estimated
(3) Based on 10 vol. % in unleaded premium base gasoline
(4) Secondary Butyl-Alcohol (SBA)
(5) Research Octane Number (RON), Motor Octane Number (MON) (See Section 4.2.1)

1.3 BLENDING OF OXYGENATES - GUIDELINES

Both in Canada and the USA, governmental agencies have established guidelines on the use of oxygenates in gasoline (limits have been set as to the quanity of oxygenates that could be blended into the gasoline pool).

1.3.1 EPA Guidelines

In the United States the Clean Air Act with ammendments requires waivers from the Environmental Protection Agency (EPA) before any octane improver, which is physically different from hydrocarbons, could be blended into unleaded gasoline. The Act does not require waivers for the blending of oxygenates into leaded gasoline.

The commonly used oxygenates approved by EPA include: EtOH, Oxinol, Arconol, MTBE, aliphatic alcohols except MeOH, propanol, butanol and aliphatic ethers, TAME and di-isopropylether (DIPE). Petrocoal blend was no longer allowed by EPA as of April 16, 1986 for not meeting the guidelines. (Petrocoal was a proprietory fuel by Anafuel Unlimited - a mixture of MeOH and certain four-carbon-alcohol in unleaded gasoline which contained up to 12 vol. % MeOH and up to 15% total alcohols). In general terms, any fuel must meet ASTM D 439 specifications. Table 1.3.1 gives the oxygenated blending agents recommended, their description and approved concentration.

TABLE 1.3.1 OXYGENATED BLENDING AGENTS APPROVED FOR USE IN UNLEADED GASOLINE IN THE USA (Source: 6 and 12)

COMPONENT	DESCRIPTION	APPROVED CONCENTRATION
Oxygenates	General rule (with the exception of Methanol)	Limited to 2 wt. %
Ethanol	C_2H_5OH	Limited to 10% (vol) in finished fuel.
OXINOL	Up to 50% MeOH in GTBA (Gasoline-Grade Tertiary-Butyl Alcohol) (Trademark of ARCO Chemical Company)	Limited to 3.5 wt % oxygen in finished fuel.
OXINOL 50	50% MeOH and 50% GTBA (Trademark of ARCO)	Limited to 3.5 wt % oxygen in finished fuel, approx. 9.5 vol % max. depending on gaoline density.
ARCONOL	GTBA with no methanol but contains small amounts of acetone, butenes, etc. (Trademark of ARCO)	Limited to 3.5 wt % oxygen in finished fuel, approx. 16 vol % depending on gasoline density.
Du Pont Blend	A mixture of MeOH and one of or a combination of EtOH, Propanol or Butanol (including GTBA) plus Du Pont't corrosion inhibitor DGOI-100.	Limited to 3.7 wt % oxygen in finished fuel and limited to a max. of 5 vol % MeOH and a minimum of 2.5 vol % cosolvent.
MTBE	Methyl-Tertiary-Butyl Ether ($C_5H_{12}O$)	Limited to 2 wt % oxygen in finished fuel, approx. 11 vol. % depending on gasoline density.
Other Aliphatic Alcohols and Aliphatic Ethers	Propanol (C_3H_7OH) Butanol (C_4H_9OH) etc. except MeOH TAME ($C_6H_{14}O$) THME ($C_7H_{16}O$) DIPE ($C_6H_{14}O$)	Limited to 2 wt % oxygen in finished fuel. Vol % depends on alcohol/ether density and gasoline density.

1.3.2 CGSB Standards - Oxygen Content

In Canada, the guidelines for oxygen content were set by the Canadian General Standards Board. The oxygen content is for a blend with unleaded automotive gasoline. Table 1.3.2 gives the specificiation values of the oxygenates both in volume % and weight %.

TABLE 1.3.2 CGSB STANDARDS FOR OXYGENATED UNLEADED AUTOMOTIVE GASOLINE - OXYGEN CONTENT (Source: 1 and 3)

Oxygenate by Volume	Oxygenate by Weight (%)
10% Ethanol (EtOH)	3.72
5% MeOH / 3% EtOH	3.80
4.75% MeOH / 4.75% IPA	3.89
4.75% MeOH / 4.75% TBA	3.64
7% MeOH / 3% IPA	4.60
5% MeOH / 3% TBA	3.37
11% MTBE	1.99

1.3.3 EEC Limitations on the Use of Oxygenates

The European Fuel Oxygenates Association (EFOA) recommended limitations on the use of oxygenates in automotive gasoline to the EEC. These limitations have been certified by the European Economic Community and are summarized in Table 1.3.3.

TABLE 1.3.3 EEC LIMITATIONS ON THE USE OF OXYGENATES (Source: 14)

Volume	Limit A (Lower Obligatory Limit)	Limit B (Upper Limit Without Labelling)
MeOH (must add suitable stablizing agents)	3	3
EtOH (stablizing agent may be necessary)	5	5
Isopropyl Alcohol (IPA)	5	10
Tert-Butyl Alcohol (TBA)	7	7
MTBE (and other ethers with a BP below 205°C and containing 5 or more C atoms per molecule)	10	15
Other defined organic oxygenates	7	10
Organic oxygenate mixtures, oxygen by weight	2.5	3.7

1.3.4 Other Gasoline Blending Additive

Methylcyclopentadienyl manganese tricarbonyl (MMT) has been used as an alternative to lead alkyls. However, its use has caused several environmental pollution problems. For this reason, it has been banned in many countries and its application is increasingly being restricted in countries where it is not banned.

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CHAPTER TWO

REACTION FUNDAMENTALS, CATALYSIS AND KINETICS

2.0 REACTION FUNDAMENTALS, CATALYSIS AND KINETICS

Methyl ethers of branched alcohols, eg. tert-butyl alcohol, ter-amyl alcohol, have found a broad application as gasoline additives. They have a high octane number (RON above 100) and, in the near future, they may replace lead based octane enhancers.

From the technological point of view, methyl-tert-butyl ether (MTBE) could be produced on a large scale using different C_4 fractions from the refinery. For this reason the major part of research on catalysts, reaction kinetics and etherification reaction mechanism was devoted to the synthesis of this compound.

2.1 THERMODYNAMICS

The equilibrium reaction for forming MTBE can be represented as follows:

$$(CH_3)_2C = CH_2 + CH_3OH \rightleftharpoons (CH_3)_2CH - CH_2 - O - CH_3 \qquad (2.1)$$

This reaction is exothermic; therefore, the equilibrium is shifted to the right at low temperatures and to the left at high temperatures. In all industrial processes the reaction is carried out in the liquid phase. Classical methods of thermodynamics allow the computation of the gas phase equilibrium constant, but for the reaction in the liquid phase, the knowledge of the liquid phase activities for all components of the reaction mixture is necessary. Colombo et al. undertook efforts to predict the activity coefficients using UNIFAC estimate (1) and standard free energy of formation values for all components. Table 1 summarizes the thermodynamic data for gas phase equilibrium.

TABLE 1.0 THERMODYNAMIC DATA FOR THE COMPONENTS FOR MTBE SYNTHESIS (1)

COMPONENT	H^o_{298} kJ/mol	G^o_{298} kJ/mol	Cp^o_{298} J/mol*K
Isobutene	-16.91	58.10	89.16
Methanol	-201.14	-162.46	43.91
MTBE	-283.61	-117.38	136.03
MTBE formation	-65.56	-13.02	

The calculated values of the enthalpy of reaction is higher than that given in other sources which are in the range of -40kJ/mol (2).

2.2 REACTION MECHANISM

In most cases, MTBE is produced during a catalytic reaction between isobutene and methanol. This etherification reaction is a methanol addition step to the double bond in the iso-butene molecule. The reaction mechanism reported in several papers involves the participation of acid sites. To catalyze the reaction of MTBE synthesis, a catalyst should have strong Broensted sites able to form solvated protons, eg., $CH_3OH_2^+$, or to form carbocations by direct protonation of iso-butene.

According to different sources, the formation of MTBE on the surface of solid catalyst has been explained in a similar way as the homogeneous acid catalyzed reaction and it includes several steps (3, 4, 5, 6), shown below:

$$C_4(1) \rightleftharpoons C_4(a) \tag{2.2}$$

$$CH_3OH(1) \rightleftharpoons CH_3OH(a) \tag{2.3}$$

$$CH_3OH(a) + H^+ \rightleftharpoons CH_3OH_2^+(a) \tag{2.4}$$

$$CH_3OH_2^+(a) + C_4(a) \rightleftharpoons CH_3OH(a) + C_4H^+(a) \tag{2.5}$$

$$C_4H^+(a) + CH_3OH(a) \rightleftharpoons MTBE(a) + H^+ \tag{2.6}$$

$$MTBE(a) \rightleftharpoons MTBE(1) \tag{2.7}$$

As proton acidity plays the most important role during the formation of MTBE, it indicates which kind of catalysts would be suitable for its synthesis. The overall reaction of MTBE formation has a slight exothermic effect of about 40kJ/mol and the equilibrium is more favourable for MTBE formation at low temperature, as the reverse reaction becomes more noticeable with rising temperatures. The MTBE synthesis equilibrium is shifted towards MTBE formation, especially at low temperatures (below 100°C) where a high conversion could be obtained (up to 98%).

The formation of tert-butyl alcohol TBA as a by-product is negligible as long as the feedstocks are thoroughly dried.

The kinetic study of the reaction of MTBE synthesis in a heterogeneous system was described for different catalysts. It was found that reaction kinetics followed the Langmuir-Hinshelwood type model. For concentration of methanol higher than 1 mol/liter, the reaction rate constant is independent of the methanol concentration and the methanol/iso-butene ratio. When the methanol concentration decreases then the increase in the rate constant was substantial (7). This suggests that a lower methanol concentration modifies the catalyst proton activity.
More information about reaction kinetics is given in Section 2.4 of this report.

The activation energy of MTBE synthesis varies,depending upon the catalyst used, from 25 kJ/mol for Amberlyst 15 to 103.4 kJ/mol for homogeneous reaction with paratoluene sulfonic acid (3, 7, 8).

The same acid catalysis reaction mechanism governs the formation of other ethers such as TAME or methyl-hexyl ethers. The only difference is in the more complex picture of chemical transformations because different isomerization reactions may occur (9).

A new approach was indicated by Bayer AG in which their laboratory developed a new bi-functional catalyst ion exchange resin-based (33). This catalyst contains not only acid sites, but also sites containing transition metals which are active in isomerization reactions. In this way, all unsaturated C_4 fractions may be converted into MTBE.

2.3 CATALYSTS

2.3.1 Resin Based Catalysts

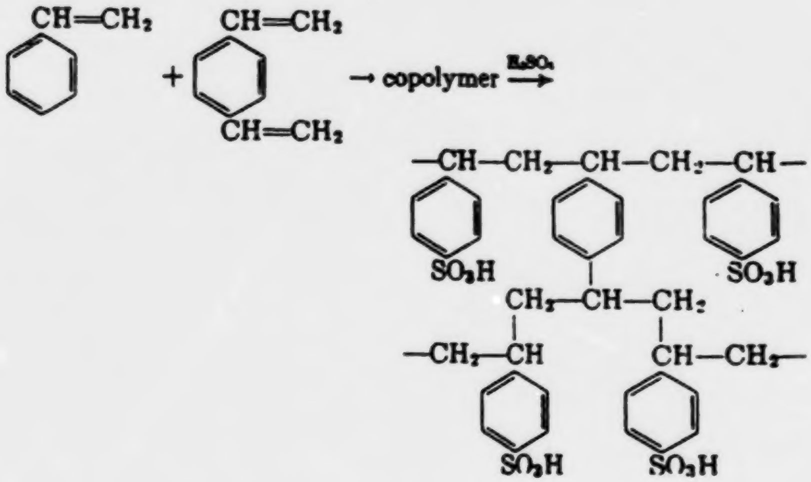
Organic polymers and especially sulfonated styrene-divinylbenzene resins, at present, are considered to be the best solid catalysts for the production of MTBE from iso-butene and methanol. Several commercial technologies have recommended Amberlyst resin as the most powerful catalyst, having a long life time and showing high selectivity of MTBE formation. This resin, with the commercial name Amberlyst 15, was the most extensively studied; however, the catalytic properties, in the reaction between iso-butene and methanol, of several other sulfonated styrene-divinyl benzene were also investigated.

2.3.1.1 Chemical Characteristics

According to reaction (2.4), the proton acidity of a catalyst is the key factor for the transformation of iso-butene and methanol into MTBE. The catalyst should be able to protonate the methanol molecule, which then interacts with iso-butene producing iso-butyl cation. This iso-butyl cation undergoes a chemical reaction with methanol-producing MTBE and regenerates the proton.

Following the above general description of the catalyst, it is evident that a good catalyst should demonstrate strong acidity. It is known from organic chemistry that concentrated sulfuric acid has a high protonating ability (pKa -7.2) and could be used as a catalyst in several acid catalyzed reactions. Its high corrosive properties and the formation of side products (iso-butene dimers and high oligomers) caused new catalyst systems to be developed, especially solid catalysts for heterogeneous reactions. At present the most extensively used resin is referred to as macroreticular sulfonated styrene-divinyl benzene resin.

Ion exchange resins suitable for catalytic applications are composed of long chains of polystyrene, locked together by means of divinylbenzene crosslinks into a three dimensional, insoluble polymeric phase called the matrix. The various resins differ in divinylbenzene content and in the nature and concentration of acid or base moities per unit volume. The general scheme for the manufacture of the ion exchange resins is shown below:



Resins can be divided into two groups, gelular and macroreticular resins, having major structural differences. Both types are briefly discussed in the following section.

2.3.1.1.1 Gelular Resins

The application of the name gelular to describe a general class of ion exchange resins could be misleading. This name refers to rigid transparent spherical beads. The three dimensional polymeric gelular matrix is a homogeneous structure. Totally dry gelular resin has the polymeric matrix collapsed and the polystrene chains are as close as the atomic forces allow. In this condition, the matrix is completely impervious to any molecule incapable of acting as a swelling medium. In this case only the collapsed gelular bead surface would be accessible to reacting molecules and the resin does not exhibit any practical catalytic activity. Catalysis by gelular resins requires the use of a swelling medium which is capable of expanding the polymeric matrix so that the solvent-filled spaces are created between polystyrene backbone chains of the matrix. These spaces constitute the microporous structure of the gelular phase.

Gelular resins are characterized by divinylbenzene content below 12%. Higher content of the crosslinking agent causes that matrix to exhibit great resistance to swelling; hence, these resins are poor catalysts.

2.3.1.1.2 Macroreticular Resins

The necessity for matrix expansion has been a limiting factor in the utilization of gelular catalysts. This inconvenience was eliminated when new types of resins were developed. These new resins have a heterogeneous structure. They consist of agglomerates of small gelular microspheres, having a microporous structure, but the gelular beads have a small diameter. The agglomerates are prepared by microspherical fusion. During this procedures new larger pores are formed between the microspheres of gelular phase. Thus macroreticular resins have areas of microporous gel matrix interspersed with macropores. The significant catalytic consequence is that whereas gelular resins can only function effectively as catalyst in a swelling medium, macroreticular resins are effective catalysts in all solvents.

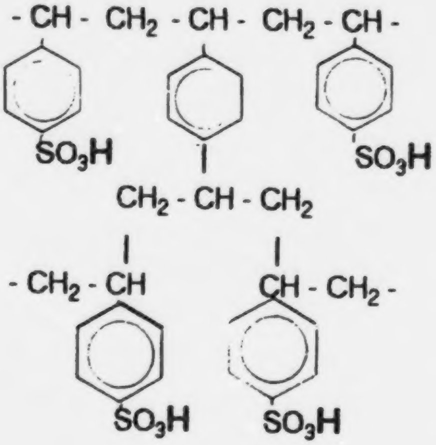
The macropore structure and particle size of macroreticular resins can be controlled during its manufacture.

2.3.1.2 Surface Properties

Acid properites of the surface of macroreticular sulfonated styrene-divinyl benzene resins are identified with the surface sulfonic acid groups. The active $-SO_3H$ group shows strong protonating properites, similar to those of pure H_2SO_4.

The concentration of sulfonic groups has a strong impact upon the catalytic properites and the reaction rate is proportional to the concentration of "active groups" (18, 34, 35, 36, 37). This means that if a resin is partially neutralized so that $-SO_3H$ groups are partially replaced with $-SO_3Na$ groups uniformly throughout the whole polymeric mass, the catalytic activity will decrease (15,38). Some deviation from this correlation was observed in the case of the reaction between methyl-butenes and methanol producing TAME. It was found that not all surface acidic centers are accessible to the reacting molecules and the reaction rate depends upon the concentration of these accessible acidic groups (39).

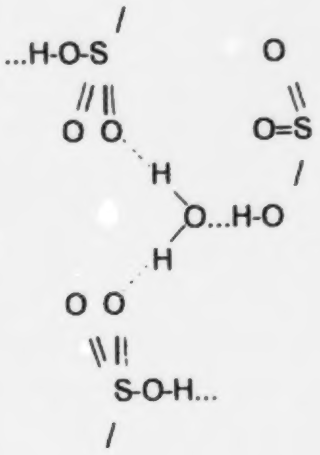
The following structure of the surface of styrene-divinyl benzene resins is considered as the active centers:



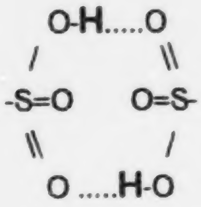
where H is an active proton

The NMR data of the intereactions between macroreticular resins and water molecules is discussed by L. Frankel (40). It is clearly shown that water in the pores or in gel phase undergoes strong interaction and proton exchange with the acidic protons of the resins. Therefore, depending upon the resin water content, two major types of catalytic reactions can be identified. The first catalytic system is characterized by the presence of sufficient amount of water to solvate all the protons contained in the sulfonic acid group causing the solvated protons to act as the active species.

In the absence of water the undissociated sulfonic acid groups will act as catalytic centers. The two possible surface structures are shown below:



I (aqueous medium)



II (dry form)

There are a number of controllable factors which can influence the catalytic properites of styrene-divinyl based ion exchange resins. These are:
- level of cross-linking;
- porosity and surface area;
- particle size;
- sulfonic acid content.

These variables may have different effects depending upon the rate determining step.

It was found from different catalytic reactions (18, 41) that increased cross-linking for gelular resins decreases the reaction rate. However, the reaction rate of macroreticular porous resins changes only to a small degree.

It has also been established that the rates of a variety of reactions are not directly proportional to the surface area of the catalyst (16, 18, 42). Therfore, the catalytic activity of a macroreticular resin depends upon both the surface sulfonic groups and the groups within the gelular portion of the solid matrix (43).

In the case of macroreticular resins the particle size does not affect the reaction rate (18) which is different in the case of gelular catalysts. In gelular catalysts, the mass transport effect through the gel phase has an impact on the catalytic reaction kinetics thereby indicating that smaller particles are more suitable for catalytic application.

Ion exchange styrene-divinyl benzene sulfonated resins undergo a desulfonation reaction (18, 19) similar to the reactions of other organic compounds (20). The rate of the desulfonation reaction depends upon temperature and increases with the increase of the former. However, other reactions leading to the neutralization of the surface acidic groups are also possible; and, in this case, the formation of sulfones was observed (19). To avoid this inconvenience, Rohm & Haas does not recommend the utilization of Amberlyst resins above 120°C.

2.3.1.3 Catalytic Properties

In addition to their ion exchange properties, sulfonated resins found application as catalysts for several acid catalyzed reactions. Depending upon the nature, in general, and the overall acidity and strength of the surface centers, in particular, different styrene-divinyl benzene resins were developed and are commercially available (5, 9, 10, 11, 14, 15, 16, 44). Specifically, the broad applications of Amberlyst, Nafion and Lewatit resins have been reported in literature.

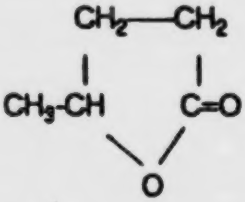
It has been reported that sulfonated styrene-divinyl benzene resins are used as catalysts for the following reactions:

- esters formation by reaction of acids and olefins

$R_2C{=}CH_2 + R'COOH \rightarrow R'{-}COOH{-}C(R)_2{-}CH_3$

- lactonization of (beta-gamma or gamma-delta) unsaturated acids

$CH_2{=}CHCH_2CH_2COOCH_3 + CH_3COOH \longrightarrow$



- alkylation of aromatic hydrocarbons and phenols (45)

$C_6H_6 + CH_2{=}CH{-}CH_3 \rightarrow C_6H_5{-}CH(CH_3)_2$

- polymerization and isomerization of olefins (46)

- alcohols dehydration (t-butanol) or olefins hydration (47)

$CH_2{=}CH{-}CH_3 + H_2O \rightarrow CH_3{-}CH(OH){-}CH_3$

- decomposition of cumene hydroperoxide

$$Ph\text{-}C(CH_3)_2OOH \xrightarrow{H^+} (CH_3)_2CO+PhOH$$

- acylation of olefins

$$CH_2{=}C(CH_3)R+(CH_3CO)_2O \longrightarrow CH_3COCH{=}C(CH_3)R+CH_3COOH$$

- condensation reactions involving activated aromatic compounds

$$PhOCH_3+(CH_3CO)_2O \longrightarrow p\text{-}CH_3OPHCOCH_3+CH_3COOH$$

- condensation of aldehydes and ketones

$$2CH_3\text{-}CO\text{-}CH_3 \longrightarrow CH_3\text{-}CO\text{-}CH_2\text{-}C(OH)\text{-}(CH_3)_2$$

- esterification in ahydrous media

$$PhOH+(CH_3CO)_2O \longrightarrow CH_3COOPH+CH_3COOH$$

- preparation of ethers by reacting of alcohols and olefins

$$(CH_3)_2C{=}CH_2+CH_3OH \longrightarrow CH_3\text{-}O\text{-}C(CH_3)_3$$

Amberlyst 15 and Lewatit are actually the most widely used macroreticular resin catalyst for MTBE synthesis. The following table lists their typical properties:

		Resin	
		Amberlyst 15	Lewatit SPC 118
Matrix crosslinking	%	20	18
Bulk density	g/l	608	700-800
Surface area	m^2/g	50	40
Average pore diameter	A	240	650
Porosity	ml/ml	.36	.25
Hydrogen ion concentration	meq./g dry	4.7	4.5

The formation of ethers from methanol and corresponding olefins competes with the isomerization reactions. Isomerization which does not occur in the case of iso-butene has a more important effect in the case of higher olefins,such as pentenes or hexenes (9, 39, 44, 48).

It was concluded that:

- only olefins having a double bond attached to the tertiary carbon atom undergo etherification;
- the etherification of alpha-olefins is faster than that of beta-olefins;
- the isomerization of alpha olefins is faster than that of beta-olefins.

For the interpretation of results both factors (thermodynamic and kinetic) should be taken into consideration. At a lower temperature range the etherification progresses with a higher selectivity, but as the reaction temperature increases isomerization begins to be competitive, thereby decreasing the selectivity of etherification. In some cases the effect of steric hindrance has to be taken into account as it was observed for the etherification of 2-methyl-pentene-1 and 2,3 dimethyl-butene-1 (9).

2.3.1.4 Resin Based Catalysts Having Improved Activity and Stability

Rhom & Haas Co. has been working on the development of new sulfonated macroreticular resins that would have better properties than the commercially used Amberlyst 15 resin. The described resins (18), according to the authors, have improved the thermal stability compared to the commercial product. However, their application for the etherification reaction was less successful because of the lower selectivity of iso-butene conversion to MTBE.

These new catalysts have a smaller surface area than Amberlyst 15 and a lower porosity. The paper did not give any indication regarding their structure or chemical composition. It would be expected that these more stable resins are less crosslinked than Amberlyst 15.

2.3.1.5 Advantages and Disadvantages of Resin Based Catalysts

Ion exchangers are particulate acids or bases and when used as catalysts offer the chemical benefits of homogeneous catalysis combined with the physical and mechanical benefits of heterogeneous catalyst systems.

When a resin is used as an acid catalyst the acidity of the active sites are more uniform than that of other inorganic catalysts such as oxides or zeolites because of its chemical structure. Although the acid strength of resin based catalysts cannot reach the low pKa values of other inorganic solids, it means that the application of macroreticular resins as a catalyst is limited.

Anhydrous macroreticular resin can be employed in non-aqueous systems, thus permitting reactions not possible with aqueous acids or bases. The product of such a reaction is isolated dry.

The loss of catalytic activity of resin catalyst may be two-fold:

- The deactivation by protons exchange with trace ions in the reactant. This deactivation can be easily eliminated by better purification of the feedstock and the resin activity may be restored by the washing procedure;
- The deactivation by organic foulants. This contamination, depending upon the nature of formed polymer, could be more difficult to handle. Usually organic foulants are removed by washing with the appropriate solvents.

The major disadvantage of ion exchange resins as catalysts is their temperature degradation. Gelular cation exchange resins in the acid form could be used up to $125^{\circ}C$ while maintaining their properties. Macroreticular resins are slightly more resistant and they can operate at $150^{\circ}C$ for an extended period of time.

The deactivation of ion exchange resins is caused by desulfonation which occurs beyond $175^{\circ}C$. The desulfonation is also a catalytic reaction catalyzed by matrix-bound $-SO_3H$ or by H_2SO_4 produced by hydrolysis of these groups.

Another disadvantage of the ion exchange resins is their high cost. Homogeneous acids or bases are several times cheaper than polymers. Research is continuing into the high cost factor in the development of new catalyst and less expensive and more stable catalysts are being sought.

2.3.2 Inorganic Catalysts

The limited lifetime and variations in catalytic properties due to the loss of the acidic character of macroreticular resins caused the initiation of research into new catalytic systems for MTBE synthesis. From the chemical point of view the surface of these new catalysts would have acidic properties, a porous structure which would not affect the reaction kinetics, and their thermal resistence would be higher than that of sulfonated sytrene-divinyl benzene resins.

These conditions may be fulfilled by several inorganic solids: amorphous oxides or mixed oxides, synthetic or natural zeolites, clays and heteropolyacids. In addition, these potential catalysts would be less expensive than synthetic resins.

It has been known for more than 30 years that some of the natural or synthetic silicates, zeolites or clays have strong acidic properties and they are able to catalyze different chemical reactions. The open, three-dimensional framework structure, large pore size (up to 8A) and high thermal and hydrothermal stability of zeolites with the faujasite structure contribute to the wide use of these materials in the preparation of petroleum cracking catalysts. However, the limited range of their pore size (from 2 to 8A) confines the utility of zeolites as catalysts for the conversion of high molecular weight compounds and occasionally, their very high activity initiates different undesireable side reactions.

Recently, a new class of molecular sieve-like materials with a larger pore-size range (from 6 to 40A) larger than faujasite-type zeolites has been synthesized by interlayering expandable clay minerals with large cations. These pillared or interlayered montmorillonite-based solids have been studied as potentially new catalysts. Papers describing the results of their use for MTBE synthesis have been published.

2.3.2.1 Clay Based Catalysts

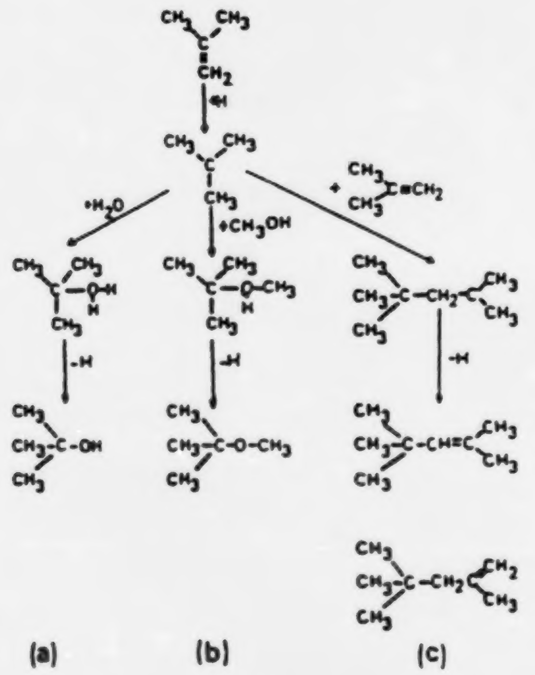
Clay based catalysts have been studied in different organic reactions (3, 21, 22, 23, 24, 25, 48, 49). It was found that interlamellar water molecules are strongly polarized and catalytically active manifesting Broensted acidity (23, 25, 50), therefore its acidity could be modified by ion-exchange. The introduction of divalent or trivalent metal ions into the clay structure causes stronger polarization of the interlayer water and stronger acidity (49). Another solution has been proposed by BP in the European Patent Application (21) for increasing the clay catalysts' acidity and activity. According to this patent, the catalyst activity was enhanced by the addition of a strong acid such as H_2SO_4, H_3PO_4, HCl and HF in the amount of 2% by weight, based upon the total weight of the reactants. In ion-exchanged montmorillonites below 100°C, the interlayer cations are fully hydrated and the clays behave only as weak acids. At 150 - 180°C these cations are not fully coordinated by water (hydrated) exercising a stronger polarizing force on the remaining water molecules causing the clays to behave as stronger acids with the ability to generate primary and secondary carbocations.

Using clay catalysts, it was found that the kinetics of MTBE formation depends on the nature of the solvent. When acidity is required then saturated hydrocarbon solvents are more efficacious (49).

2.3.2.1.1 MTBE Synthesis Over Clay Catalysts

In 1980, Bylina et al. (25) indicated that the synthesis of MTBE in the presence of metal-exchanged montmorillonite is possible at 95 - 100°C with a 70% yield. Several different olefinic hydrocarbons were formed as the side products under these conditions. It was found that the formation of MTBE depends upon the solvent used and the best results were achieved in 1,4-dioxane (22, 23).

Adams compared montmorillonite-derived catalysts with the Amberlyst 15 resin (3). He concluded that sulfonated resins have a 50% higher activity than the activity of ion-exchanged clays and having a similar proton acidity to Amberlyst 15 (4.5 mmole H_2O/g of clay). The formation of different by-products was observed in the presence of clay catalysts . The mechanism of Adams' (22) proposal for the production of t-butanol, MTBE and 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 is shown below:



Mechanism of the production of (a) t-butanol, (b) methyl t-butyl ether, and (c) 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene.

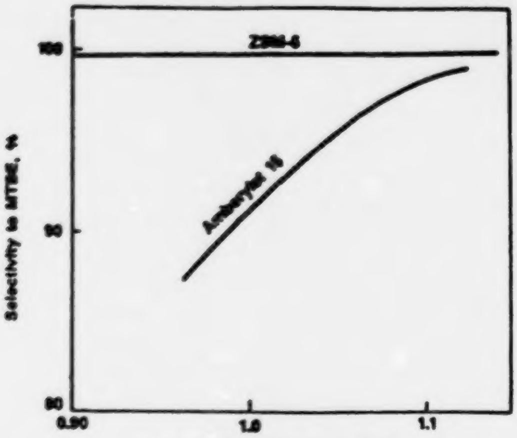
In conclusion, the potential use of clays or pillared clays as catalysts for MTBE synthesis requires more fundamental research. At present, these solids cannot compete with sulfonated resin based catalytic systems.

2.3.2.2 Zeolite Based Catalysts

In 1981, Mobil Oil (29) and in 1982, ICI (28) obtained European Patents for the utilization of zeolites as catalysts for the production of ethers using different olefinic streams in a refinery. The ICI Patent indicates that the zeolite structure influences very strongly the iso-butene conversion to MTBE. Similar conclusions were drawn in recent publications (26, 27).

The Russian produced zoelite Ceokar-2 showed activity in the broad range of pressures (from 1 to 2.5MPa) and temperatures from (80 to 150^{o}C) when gaseous C_4 products from the FCC unit came into contact with methanol (26). Modification of this zeolite with manganese decreased its activity significantly. A higher pressure and a higher temperature was required.

Chu and Kuhl identified HZSM-5 and HZSM-11 to be highly active and selective for the preparation of MTBE (27). Both selected zeolites were compared against the commercial catalyst, Amberlyst 15 resin. As a result of the shape-selective properties, ZSM-5 gave a superior selectivity to MTBE over the entire range of methanol to iso-butene ratios compared with Amberlyst 15 catalyst whose selectivity approaches that of ZSM-5 only at high $CH_3OH/i\text{-}C_4H_8$ (Figure 1).



Liquid-phase selectivity to MTBE vs. $CH_3OH/i\text{-}C_4H_8$

The authors of these papers have shown an example of the application of zeolitic catalysts performing at low temperatures. Both zeolites gave the following advantages over the commercial catalyst, Amberlyst 15 resin:

- high thermal stability;
- high selectivity to MTBE and lower formation of by-products;
- lower sensitivity to the methanol/iso-butene ratio;
- even at higher temperatures (thermodynamically unfavourable conditions), the process can be performed with the zeolite catalyst;
- zeolite catalyst may be periodically regenerated.

If in the near future a catalyst replaces the sulfonated macroreticular resins for MTBE or TAME synthesis, it will probably be a zeolite based system. Recent progress in the development of new crystalline silicates may bring a new catalytic system which may have very high activity and selectivity at low temperatures.

At present Amberlyst 15 gives higher conversion than zeolites at a lower temperature range. When $CH_3OH/i\text{-}C_4H_8$ ratio is above 1.1, the selectivity of both catalysts to MTBE formation is comparable. The commercial use of zeolites awaits further improvements.

2.3.2.3 Other Catalysts

Heteropolyacids have been known as solids having an acidic surface. For this reason they were selected for testing as potential future catalysts of MTBE synthesis (30,31). It was found that 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) (TPE), 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) (MPA), 12-molybdosilicic acid ($H_4SiMo_{12}O_{40}$) (MSA), 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$) (TSA) and their metal salts are catalytically active in gas phase reaction between methanol and iso-butene.

The acidity of these catalysts may be associated with water coordinated to metal cations (Mn^+) yielding protons by the following reactions:

$$Mn^+ + mH_2O \longrightarrow [M(H_2O)_m]^{n+} \longrightarrow [M(H_2O)_{m-1}(OH)]^{(n-1)+} + H^+$$

It was also concluded (30) that silver (1) and copper (11) salts of TPA and TSA are as active as pure heteropolyacids producing MTBE even with higher selectivity but under one condition - these catalysts should be pretreated with hydrogen or hydrogen should be present in the reacting gas mixture. This fact is explained by the formation of acid sites according to the reaction:

$$Ag(1) + 1/2H_2 \longrightarrow Ag^o + H^+$$

In spite of the high selectivity (about 100%) the hetropolyacid based catalyst have lower activity than the activity of sulfonated resins, clays or zeolites.

At present the commercial application of heterogeneous catalysts belonging to this class of solids seems to be rather doubtful due to their low activity in the range of temperatures between 40°C and 80°C.

Suzuki and Ono tried to synthesize silica based catalysts containing sulfo groups -Si-O-R-SO3H (51). These catalysts were active in dehydration of iso-propyl alcohol and in the reaction between iso-butene and methanol. The selectivity of propylene in the first reaction, and of MTBE in the second reaction, was high but the overall activity was significantly lower than macroreticular resin based catalysts.

Two other papers deserve to be mentioned here. One published by Bayer AG (33), reporting the development of bifunctional resin catalyst. This catalyst allows for MTBE production and for removing by-products such as diolefins, acetylenes and carbonyl compounds in the same reactor in the presence of hydrogen. This new bifunctional catalyst is a macroporous strong-acidic sulfonated resin with less than 5 g/liter palladium. The palladium is fixed in a special process to the resin beads in a finely dispersed form.

In the other publication by Russian authors (32), MTBE is produced from iso-butene or tert-butylalcohol and synthesis gas over Cr_2O_3 supported on a wide pore solid support, according to the following reaction:

$$(CH_3)_3COH + CO + 2H_2 \xrightarrow{300C} (CH_3)_3COCH_3 + H_2O$$

Somehow, the reaction of MTBE formation does not reach a high selectivity; this approach allows the elimination of the methanol synthesis step. It may be worthwhile to follow progress in this area.

2.3.3 Catalysts for Ether Synthesis - Conclusions

Among the whole variety of catalysts tested for the reaction of olefins etherification, only one group has found commercial application. These are catalyts based upon sulfonated styrene-divinylbenzene macroreticular resins.

The old technology using sulfuric acid as a catalyst has been abandoned as not being selective enough and causing corrosion problems.

As resin based catalysts are not free of weak points, further research has been in progress. The main focus in the development of new catalysts is directed at systems that are more stable at higher reaction temperature, on easier regenerable and on lower cost catalysts. Macroreticular resin cost is high compared to other catalysts. As a result of this, resin cost could be considered as part of investment costs rather than plant operational cost.

Research results show that until now the application of inorganic based catalysts is not justified due to their lower activity and especially lower selectivity. The lower selectivity is caused by several side reactions resulting from the non-uniformity of acid sites on the catalyst surface. We would expect that with the recent progress in the synthesis of new crystalline zeolites an effective inorganic catalyst will be developed in the near future thereby improving the economic effect of ether synthesis.

Another possible development in ethers synthesis would be the development of a catalytic system able to convert not only ramified olefins with tertiary carbon atoms, but also other olefins having secondary carbon atoms. This task requires the application of stronger acidic catalysts than those actually used in ion exchange resins. Such a new catalytic system may isomerize olefinic feedstock, therefore C_4 fractions from FCC units or pyrolysis could be directly used for increasing the raw material base for MTBE production.

2.4 REACTION KINETICS

2.4.1 Reaction Model and Kinetics

Two approaches have been broadly used by different researchers in modelling ion-exchange catalyzed reactions of C_4 and C_5 fractions.

The first approach envisions the resin to behave like a dissolved electrolyte, hence, the treatment as a homogeneous reaction in the liquid phase. In the second approach the resin is regarded as a solid porous catalyst and the reaction model is therefore treated as heterogeneous catalytic.

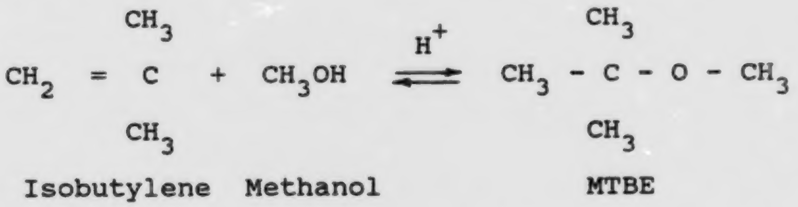
Because the reaction is carried out in commercial reactors in the liquid phase, discussions on the kinetics here are based on the liquid phase reaction. For the vapour phase reaction to produce MTBE, methanol partial pressure enhances MTBE yield (30).

2.4.1.1 Homogeneous Reaction Model

The macroreticular structure of the ion-exchange resins provides ready and easy access of liquid reactants to the hydrogen ions present all through the resin beads. There is no resistance to diffusion of reactants into the pores or products diffusing out of the pores. This implies that the concentration of the reactants in both the bulk phase and inside the pores are nearly the same. This situation is similar to that of homogeneous reactions taking place in the liquid phase. Under these conditions of no diffusion limitations, Helfferich (52) classified the liquid phase reaction of acid resin catalysts as homogeneous.

The reaction of MTBE synthesis using ion-exchange resins is reversible (see eq. 2.4.1). This implies that under suitable conditions MTBE can be decomposed to isobutylene and methanol.

(i)

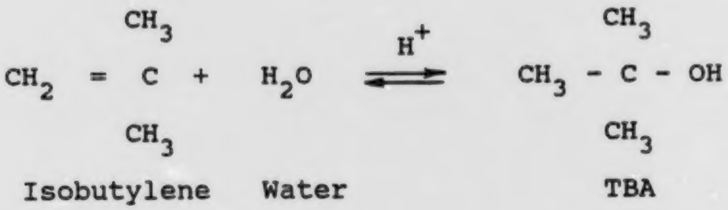


$$CH_2 = \underset{CH_3}{\overset{CH_3}{C}} + CH_3OH \overset{H^+}{\rightleftharpoons} CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - O - CH_3 \qquad (2.4.1)$$

Isobutylene Methanol MTBE

Besides the main reaction the following minor reactions take place (53) yielding some by-products.

(ii) hydration of isobutylene to tert-Butyl alcohol

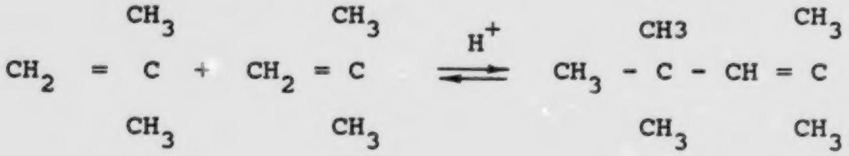


$$CH_2 = \underset{CH_3}{\overset{CH_3}{C}} + H_2O \overset{H^+}{\rightleftharpoons} CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - OH \qquad (2.4.2)$$

Isobutylene Water TBA

This reaction can be minimized by excluding water from the feed.

(iii) dimerization of isobutylene to di-isobutylene



$$CH_2 = \overset{CH_3}{\underset{CH_3}{C}} + CH_2 = \overset{CH_3}{\underset{CH_3}{C}} \overset{H^+}{\rightleftharpoons} CH_3 - \overset{\mathrm{CH3}}{\underset{CH_3}{C}} - CH = \overset{CH_3}{\underset{CH_3}{C}} \qquad (2.4.3)$$

Isobutylene DIB

(iv) loss of methanol by methanol reaction to dimethylether

$$CH_3OH + CH_3OH \overset{H^+}{\rightleftharpoons} CH_3 - O - CH_3 + H_2O \qquad (2.4.4)$$

Methanol DME Water

The main reaction (2.4.1) can be simply represented as:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \qquad (2.4.5)$$

Methanol Isobutylene MTBE

Subramaniam and Bhatia (53) derived a homogeneous kinetic model for this reaction (eq. 2.4.5) with the assumption that the forward reaction is second order and reversible. They expressed the rate of disappearance of methanol r_A as:

$$-\frac{dc_A}{dt} = k_1 c_A c_B - k_2 c_C \qquad (2.4.6a)$$

$$r_A = k_1 (c_A c_B - c_C/K) \qquad (2.4.6b)$$

and after integration and simplification in terms of fractional conversion, X, the equation becomes:

$$-\frac{\ln[c_B - (c_B - 1/K)X]}{(c_B - 1/K)} = k_1 t \qquad (2.4.7)$$

whereby:

k_1 = forward reaction rate constant (homogeneous model) $dm^3/(kmol)(hr)$

k_2 = reverse reaction rate constant (homogeneous model) $dm^3/(kmol)(hr)$

K = equilibrium constant at reaction temperature $K = k_1/k_2$

c_A = concentration of methanol ($kmol/dm^3$)

c_B = concentration of isobutylene ($kmol/dm^3$)

c_C = concentration of MTBE ($kmol/dm^3$)

Clarification of equation (2.4.6)

For a given reaction system:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C \tag{2.4.5}$$

MeOH IB MTBE

The forward reaction rate is given by:

$$r_1 = k_1 c_A c_B \tag{2.4.8}$$

The reverse reaction rate is given by:

$$r_2 = k_2 c_C \tag{2.4.9}$$

At equilibrium $r_1 = r_2$, therefore,

$$k_1 c_A c_B = k_2 c_C \tag{2.4.10}$$

$$\frac{k_1}{k_2} = K = \left[\frac{(c_C)}{(c_A c_B)}\right]_{\text{equil.}} \tag{2.4.11}$$

In view of excess methanol normally used in the reaction

$$k_1 = k c_A \tag{2.4.12}$$

whereby k is the overall reaction rate constant.

The value of k_2 can be determined from literature values of the equilibrium constant K defined by equation (2.4.11) and then making

$$k_2 = \frac{k_1}{K} \qquad (2.4.13)$$

Alternatively, one can determine k_1 and k_2 experimentally, i.e., determine k_1 and k_2 simultaneously by adjusting kinetic data with the complete equation (the intrinsic rate - rate of disappearance of isobutylene r_B),

$$r_B = kc_Ac_B - k_2c_C \qquad (2.4.14)$$

for a suitable range of MTBE concentrations. One has to be alerted, however, that the $k(k_1,k_2)$ values obtained from both methods are often not the same. For genuine reactor simulation the effects of the uncertainty in k_2 on reactor performance has to be studied.

2.4.1.2 Heterogeneous Reaction Model

If we assume that methanol and isobutylene are in the liquid phase and the resin is a solid catalyst then the reaction can be treated as heterogeneous and a Langmuir-Hinshelwood approach would apply. The successive reaction steps assumed to take place at the surface using the Langmuir-Hinshelwood Model are (see corresponding equations):

a) The adsorption of Methanol (A) and/or isobutylene on the surface of the resin (adsorption of one or both reactants);

b) Reaction between adsorbed reactants at the surface of the resin catalyst;

c) The desorption of the product (MTBE) from the surface of the resin.

$$A + B \underset{k_2}{\overset{k_1}{=\!=}} C \qquad (2.4.5)$$

Methanol Isobutylene MTBE

a) $A + s \rightleftharpoons As$ (2.4.15)

$B + s \rightleftharpoons Bs$ (2.4.16)

Adsorption of A and B molecules

b) $As + Bs \rightleftharpoons Cs + s$ (2.4.17) Adsorbed A reacts with adsorbed B on the surface (Dual site mechanism)

OR

$As + B \rightleftharpoons Cs$ (2.4.18) Adsorbed A reacts with B in the fluid, (Single site mechanism)

c) $Cs \rightleftharpoons C + s$ (2.4.19) Desorption of product C

The rate of the reaction will be controlled, however, by a single step - the slow step, while all other steps occur at the near equilibrium. Kinetic models are derived based on the regime that controls the reaction rate. Possibilities are:

- the rate of adsorption of methanol (A) controlling (step (a) above) with the reaction rate expression:

$$r = \frac{k_a(c_A - c_C/Kc_B)}{1 + K_Bc_B + K_Cc_C + K_{CB}c_C/c_B} \tag{2.4.20}$$

- the rate of surface reaction controlling (step b) with the reaction rate expressions:

$$r = \frac{k_sK_AK_B(c_Ac_B - c_C/K)}{(1 + K_Ac_A + K_Bc_B + K_cc_C)2} \tag{2.4.21}$$

Dual Site Mechanism

$$r = \frac{k_s(c_Ac_B - c_C/K)}{1 + K_Ac_A + K_Bc_B + K_cc_C} \tag{2.4.22}$$

Single Site Mechanism

- the rate of desorption of MTBE controlling (step c) with the reaction rate expression:

$$r = \frac{k_d(c_Ac_B - c_C/K)}{1 + K_Ac_A + K_Bc_B + K_CKc_Ac_B} \tag{2.4.23}$$

whereby:

k_a = adsorption rate constant $[dm^3/(kmol)(hr)]$
k_d = desorption rate constant $[dm^3/(kmol)(hr)]$
k_s = surface reaction rate constant for the heterogeneous model $[dm^3/(kmol)(hr)]$
K = equilibrium constant = k_1/k_2 at reaction temperature
K_A = Methanol adsorption equilibrium constant
K_B = Isobutylene adsorption equilibrium constant
K_C = MTBE desorption equilibrium constant
r = rate of methanol disappearance $[kmol/dm^3 hr]$

These heterogeneous reaction kinetic models postulated in (53) correspond to general reaction rate mechanisms tabulated in Perry (54).

2.4.1.3 Energy of Activation

The variation of the rate constant with temperature serves to determine the activation energy. The activation energies determined for MTBE synthesis using various catalysts are listed in Table 2.4.1.

TABLE 2.4.1 ACTIVATION ENERGIES OF MTBE SYNTHESIS
(Source: Adapted from 7)

System	Catalyst	E (kJ/mol)	Ref.
Solid/Liquid	Amberlyst 15	82.0	(7)
Solid/Liquid	Amberlyst 15	74.08	(34)
Solid/Liquid (initial rate)	Amberlyst 15	71.15	(47)
Gas (iC_4)/Liquid (MeOH)	Methyl Sulfuric Acid	87.9	(56)
Homogeneous	Methyl Sulfuric Acid	91.2	(56)
Homogeneous (initial rate)	Paratoluene Sulfonic Acid	103.4	(34)
Homogeneous Model	Amberlyst 15	79.0	(53)
Heterogeneous Model	Amberlyst 15	76.73	(53)

The above table indicates that the Activation Energy obtained with Amberlyst 15 Sulfonic Acid resins are generally lower than those obtained by using an acid in solution in the reaction mixture.

The apparent activiation energy of three commercial catalysts were calculated from experimental data by Colombo and Dalloro (13). Their results given in Table 2.4.2 are similar to the activation energies reported in Table 2.4.1.

TABLE 2.4.2 ACTIVATION ENERGY OF COMMERCIAL CATALYSTS
(Source: 13)

Catalyst Type	Activation Energy (kJ/mol)
Amberlyst 15	74.93
Kastel C 350 P	79.12
Lewatit SPC 118	79.12

2.4.1 Conversion in Etherification of C_4's and C_5's

A few papers have been published on the reaction rate of isobutene etherification to MTBE. Very little has been published, however, on the etherification of C_5 olefins. A recently published paper on the etherification of isoamylenes with Methanol (39) confirms earlier findings for isobutene etherification with methanol.

Assuming an ideal plug-flow reactor the reaction rate was defined as the number of moles converted per second per acid site according to the equation:

$$-r_i = \frac{1}{N_i} \frac{dn_i}{dt} \qquad (2.4.24)$$

whereby, N_i = number of acid sites
n_i = number of moles

Conversion of TAME in a C_5 fraction is defined as:

$$X_T = 100 \text{ X } \frac{\text{TAME (out)}}{\text{Isoamylene (in)}} \qquad (2.4.25)$$

The ratio of the amount of ether formed to that of reactive olefins in the feed gives overall conversion).

The conversion of the individual compounds was calculated as:

$$X_{2M_iB} = 100 \text{ X } \frac{2M_iB(\text{in}) - 2M_iB(\text{out})}{2M_iB(\text{in})} \quad i = 1, \text{ or } 2 \qquad (2.4.26)$$

$$X_{TAME} = 100 \text{ X } \frac{\text{TAME (in)} - \text{TAME (out)}}{\text{TAME (in)}} \qquad (2.4.27)$$

The conversion for the isomerization reaction was given as:

$$X_I = 100 \text{ X } \frac{2M_iB(\text{out})}{2M_jB(\text{out})} \quad i,j = (1, 2) \text{ or } (2,1) \qquad (2.4.28)$$

The isomerization selectivity was defined as:

$$S_I = 100 \text{ X } \frac{X_I}{X_T} = 100 \text{ X } \frac{\text{Isomerization Conversion}}{\text{Overall Conversion}} \qquad (2.4.29)$$

The studies in general agree on the following:

- two types of reactions of the olefins take place - etherification and double-bond isomerization;

- the only reactive compounds are those with the double bond attached to the tertiary carbon atom;

- the etherification of α-olefins is faster than that of β-olefins;

- the isomerization of α-olefins is faster than that of β-olefins.

- depending on the reactive olefins, at temperatures above certain values (60 - 70°C) thermodynamic factors start to control the reaction. At lower temperatures the reaction rate is more dependent on kinetic factors;

- the selectivities of the reactions (etherification and isomerization) do not depend on the amount of active sites - so, the activity of the sites are the same;

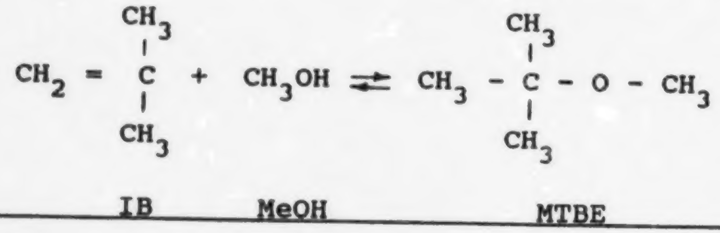
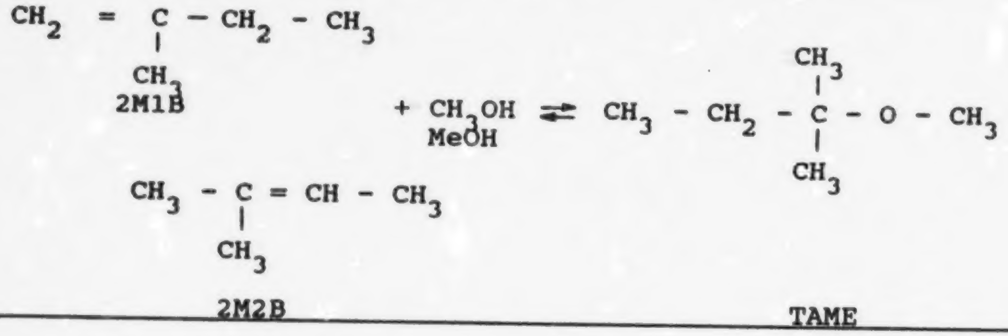
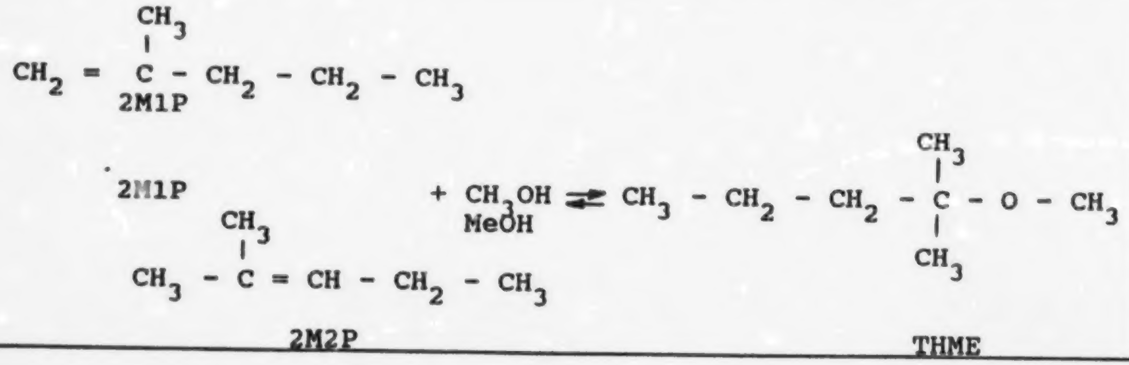
- overall conversion depends strongly on hydrogen-ion concentration which again depends on the temperature;

- reaction rates for TAME formation are slower than for MTBE

- a system designed for MTBE will also produce TAME;

- conversion in etherification decreases as you go from C_4 hydrocarbons to C_7 hydrocarbons as shown in Table 2.4.3.

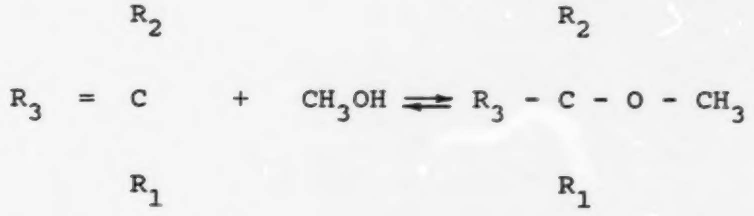
TABLE 2.4.3 DEPENDENCE OF CONVERSION ON NUMBER OF CARBON ATOMS IN THE MOLECULE (Sources: Adapted from 57 and 58)

Reaction	Source: 57	Source: 58	
	Conversion %	RON	MON
C_4:  $CH_2 = \underset{CH_3}{\overset{CH_3}{C}} + CH_3OH \rightleftharpoons CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - O - CH_3$ IB MeOH MTBE	93	118	101
C_5:  $CH_2 = \underset{CH_3}{C} - CH_2 - CH_3$ 2M1B $CH_3 - \underset{CH_3}{C} = CH - CH_3$ 2M2B $+ \underset{MeOH}{CH_3OH} \rightleftharpoons CH_3 - CH_2 - \underset{CH_3}{\overset{CH_3}{C}} - O - CH_3$ TAME	61	112	99
C_6:  $CH_2 = \overset{CH_3}{C} - CH_2 - CH_2 - CH_3$ 2M1P 2M1P $CH_3 - \overset{CH_3}{C} = CH - CH_2 - CH_3$ 2M2P $+ \underset{MeOH}{CH_3OH} \rightleftharpoons CH_3 - CH_2 - CH_2 - \underset{CH_3}{\overset{CH_3}{C}} - O - CH_3$ THME	35	100	90
C_7: $C_7 + CH_3OH$ Tertiaryheptyl methyl ether	10-20	90	77

2.4.3 Etherification of C_6 Olefins

The use of MTBE as octane boosters is extremely limited by the amount of isobutane available in the C_4 stream. Other ethers derived from C_5 and C_6 hydrocarbons have been explored as octane boosters but results indicate that they do not improve the octane number as strongly as MTBE.

The higher methyl-ethers can be prepared in a similar manner as MTBE. Olefins with a tertiary carbon atom react with Methanol to yield ethers according to the general equation:



$$R_3 = \overset{R_2}{\underset{R_1}{C}} + CH_3OH \rightleftharpoons R_3 - \overset{R_2}{\underset{R_1}{C}} - O - CH_3 \tag{2.4.30}$$

Krause et al (9) presented possible reactive C_6 hydrocarbons. Table 2.4.4 shows the reactive C_6 hydrocarbons from experimental studies reported in 2.16 and also shows the ethers formed by four of the reactive C_6 hydrocarbons. Their reaction rates and selectivities at given temperatures are also shown in the table.

TABLE 2.4.4: REACTIVE C_6 HYDROCARBONS (Reaction Rate, Selectivity and Conversion given are at 60°F) (Source: 9) Page 1 of 2

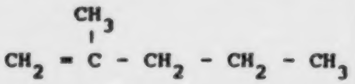
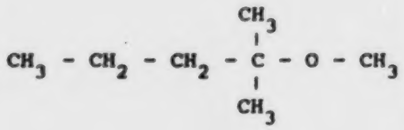
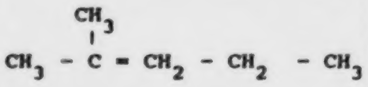
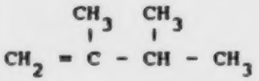
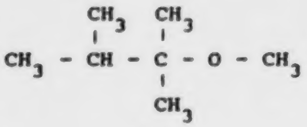
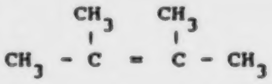
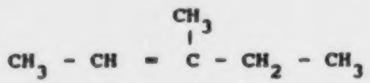
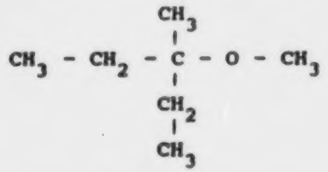
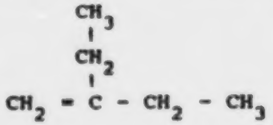
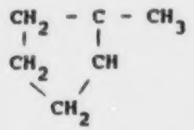
NAME	COMPOUND	ETHER FORMED	REACTION RATE $\times 10^{-3} \times mol \times (eq.\ H^+)^{-1} \times s^{-1}$			SELECTIVITY %
			Overall	Etherific	Isomer.	
2-Methyl-1-Pentene 2M1P	 $CH_2 = \overset{CH_3}{C} - CH_2 - CH_2 - CH_3$	 $CH_3 - CH_2 - CH_2 - \underset{CH_3}{\overset{CH_3}{C}} - O - CH_3$ 2-Methyl-2-Methoxypentane	3.0	2.0	1.1	66
2-Methyl-2-Pentene 2M2P	 $CH_3 - \overset{CH_3}{C} = CH_2 - CH_2 - CH_3$		1.4	1.2	0.2	88
2,3-Dimethyl-1-Butene 2,3DM1B	 $CH_2 = \overset{CH_3}{C} - \overset{CH_3}{CH} - CH_3$	 $CH_3 - \overset{CH_3}{CH} - \underset{CH_3}{\overset{CH_3}{C}} - O - CH_3$ 2,3-Dimethyl-2-Methoxybutane	3.5	1.7	1.8	50
2,3-Dimethyl-2-Butene 2,3DM2B	 $CH_3 - \overset{CH_3}{C} = \overset{CH_3}{C} - CH_3$		2.1	1.4	0.9	75

TABLE 2.4.4: REACTIVE C_6 HYDROCARBONS (Reaction Rate, Selectivity and Conversion given are at 60°F) (Source: 9)

Page 2 of 2

NAME	COMPOUND	ETHER FORMED	REACTION RATE $\times 10^{-3} \times mol \times (eq.\ H^+)^{-1} \times s^{-1}$			SELECTIVITY %
			Overall	Etherific	Isomer.	
3-Methyl-2Pentene (cis and trans) 3M2P-c, 3M2P-T	 $CH_3-CH=C(CH_3)-CH_2-CH_3$	 $CH_3-CH_2-C(CH_3)(CH_2CH_3)-O-CH_3$ 3-Methyl-3-Methoxypentane	--	--	--	--
2-Ethyl-1-Butene 2E1B	 $CH_2=C(CH_2CH_3)-CH_2-CH_3$	--	--	--	--	--
1-Methylcyclopentene		--	--	--	--	--

Results of the studies agree quite well with those carried out in C_4's-etherification, ie:

- only compounds with a tertiary carbon atom react;
- α-olefins' etherification if faster than that of β-olefins;
- α- olefins isomerization is faster than that of β-olefins;
- the compounds 2M1P and 2M2P have the same reaction scheme. Both compounds are assumed to form a common intermediate which either isomerizes or forms the ether according to the scheme:

$$\begin{tikzcd}
\text{2M1P} \arrow[dr, shift left=0.5ex] & & \\
& X \arrow[ul, shift left=0.5ex] \arrow[dl, shift left=0.5ex] \arrow[r, shift left=0.5ex, "+\ CH_3OH"] & \text{THME} \arrow[l, shift left=0.5ex] \\
\text{2M2P} \arrow[ur, shift left=0.5ex] & &
\end{tikzcd}$$

(Tertiary-Hexyl-Methyl-Ether)

(2.4.31)

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CHAPTER THREE

PROCESSES AND TECHNOLOGIES

3.1 C_4 TECHNOLOGIES

It is said that there is a "renaissance in C_4 chemistry" (2). About 20 years ago, C_4 compounds were favoured feedstocks for the chemical industry (butanes and butenes). In the late 1960's and later, chemical producers tended to move towards lighter feedstocks. Lately, a decline in C_4 market value has spurred renewed interest in C_4's. In August 1987, the American Institute of Chemical Engineers, at a meeting in Minneapolis, dedicated two sessions to papers and discussions on the upgrading of C_4's. Speakers at the meeting outlined novel schemes. All in all, the individual companies have more and more specific requirements. Although other possible products from C_4's would be mentioned, the main emphasis in dealing with technologies shall be those technologies which process C_4's to oxygenates, preferentially MTBE.

SOURCES OF C_4'S

There are three main sources of C_4 hydrocarbons:

1) Field Butanes - These are available in gas condensates from natural gas or associated gas, and are easily dehydrogenated to C_4 olefins. In some parts of the world, these field butanes are flared.

2) FCC Units - In the U.S.A., most of these are utilized through alkylation units and catalytic polycondensation plants.

3) Steam Crackers - In Europe and Japan, the steam cracking of naphtha or gasoil coproduces C_4's, whereas in North America, the steam cracking of ethane to ethylene coproduces C_4's.

Irrespective of the source of the C_4's, companies have always been confronted with the common problem of what to do with the C_4's. Typically, companies with a reasonable quantity of butadiene in their C_4 fraction built butadiene extraction units to extract and separate 1,3 butadiene. After such an extraction, the C_4 fraction is termed raffinate-1 (spent C_4).

The problem of what to do with the C_4's turned into what to do with raffinate-1. Because of the varying nature of the composition of the spent C_4 (from one company to another), each company had to look for a way of solving its problem. This individual approach has led to the existence of different processes.

With increased use of oxygenates in the unleaded gasoline pool, many of the companies transformed their raffinate-1 into MTBE. In this etherification process, methanol is normally removed together with the unreacted C_4's. These are separated in a waste wash tower whereby H_2O and methanol are removed from the bottom of the tower and a C_4 raffinate is removed from the top. This other spent c_4 is termed raffinate-2. Different companies have found ways of utilizing the raffinate-2, thereby processing the C_4's to extinction.

3.1.1 Processing C_4'S to Oxygenates

There is an abundance of know-how and processes for the conversion of C_4's to oxygenates (octane boosters to the gasoline pool) -- MTBE. Of commercial significance, and well known amongst these process licensors are:

i) Snamprogetti/ANIC MTBE Process, (Italy)
ii) Atlantic Richfield Company (ARCO), (USA)
iii) Chemical Research & Licensing Co./Neochem Corporation, (USA)
iv) EC Erdolchemie/BP, (W. Germany/G.B.)
v) Huls A.G., (W. Germany)
vi) Deutsche Texaco, (W. Germany)
vii) Institute Francais du Petrol (IFP), (France)
viii) Hungarian Oil and Research Institute (MAFKI), (Hungary)
ix) Phillips Petroleum, (USA)
x) Suntech/Houdry, (USA)

Generally speaking, these processes are identical in that they all start with an isobutylene rich C_4 stream (raffinate-1) and through an etherification process with methanol as the co-reactant produce MTBE.

The major difference between these technologies is noted in the following:

1. Reactor Type (heat removal is important)
    - fixed bed with heat removal by external heat exchangers (most processes);
    - multi-tubular reactors packed with catalyst and cooled by water (v);
    - expanded bed reactor with external cooling (vii);
    - simultaneous reaction and distillation in a single packed bed reactor (iii).

2. Isobutene conversion level (80% to 99.8%) (depends on single or two-stage reactor system).

3. Methanol contamination (0.1 wt% to 10 wt%).

4. MTBE Purity (60% to 99.8%).

5. Methanol/Isobutene feed ratio (stoichiometric or above stoichiometric).

6. Catalyst type (commercial processes)
   - acidic ion exchange type (all other licensors);
   - sulphuric acid (MAFKI) (viii).

7. Down stream units: A main difference between various processes crops up due to the method of separation of methanol, water and unreacted C_4's from MTBE.

The reaction is run in the liquid phase and entails reacting methanol with isobutylene in the presence of sulfonated polystyrene crosslinked with divinylbenzene as a catalyst. The reaction is exothermic yielding 8.8 Kcal/mole. Most of the processes are run between 100 - 200°F. Lower temperatures favour more complete conversions and longer catalyst life but slower reaction rates. Increased heat shifts the equilibrium of the process towards starting materials, producing faster reactions at the cost of net conversion, catalyst life, and the loss of isobytylene due to polymerization. The reaction is conducted at pressures of 100 - 200 psi. Operators favour keeping to the lower side of the pressure just to keep the C_4 feedstock in the liquid phase. Pressures approaching 200 psi are needed for C_4 streams containing propylene.

All available MTBE processes generally include three sections:
- reaction;
- fractionation;
- purification.

A few of the commercial processes are described here. They include:

A) Snamprogetti/ANIC MTBE Process:
- typical of the conventional processes

B) MAFKI Process:
- with a sulfuric acid catalyst instead of the conventional ion exchange resin

C) IFP Process:
- the reactor is an ebullating bed type as opposed to a conventional fixed bed reactor

D) CR&L/NEOCHEM Process:
- reaction and distillation are carried out in one vessel, the catalytic distillation unit.

A) SNAMPROGETTI/ANIC MTBE PROCESS

Feed: C_4 streams (1):

- from steam cracking after butadiene extraction (isobutene content: 40 - 50 wt%)
- from steam cracking before butadiene extraction (no limitation on butadiene content)
- from catalytic cracking units (isobutene content: 10 - 20 wt%)
- from production wells or refineries (integration with n-butane isomerization of n-butane to isobutane, and dehydrogenation to isobutene).

Process: The feed and methanol are preheated and fed to the reactor. The reactor effluent consists mainly of MTBE, but also contains unreacted isobutene and Methanol, with butanes, linear butenes and small amounts of diisobutene and tert-butyl-alcohol (1, 2)

The reaction mixture, after being preheated with bottom product of the purification tower, is fed into a simple distillation tower. Here, MTBE is separated from the spent butenes (see Fig 3.1). The spent butenes, as the top stream, contain unreacted MeOH and are sent to a methanol recovery unit and recycled. The purification tower bottom produces MTBE gas product, MTBE content is greater than 98 wt%. When required, it is possible to obtain a product with an MTBE content higher than 99% and a C_4 fraction with less than 1% isobutene.

Reactor: The reactor is a tube bundle type with the catalyst inside the tubes. Water circulation in an external closed cycle is used to remove the reaction heat of the exothermic reaction.

Conversion: Isobutene conversion levels higher than 99.9% could be achieved.

Catalyst: Acidic ion exchange resin.

Snamprogetti claims advantages or strong points for its process over other processes. These can be summarized as follows:

- extreme flexibility of C_4 feedstock (source and composition);
- low energy intensive process (low production cost);
- wide range of isobutene conversions;
- less catalyst inventory;
- longer catalyst life;
- easy plant operability and maintainance;
- no pollution problems;
- demonstrated know-how and long commercial MTBE plant experience (licensed more MTBE plants worldwide than any other process licensor);
- proven reliability;
- wide availability of new associated technologies eg. - isomerization of linear C_4 olefins to isobutene (4);
- MTBE cracking or decomposition to isobutene (5) (16);
- high purity Butene-1 production from C_4 raffinate of an MTBE unit (4);
- purification of MTBE to high purity (7);
- ease of integration within existing facilities.

Snamprogetti also prides itself on building the first commercial MTBE plant in the world - a 100,000 t/yr MTBE production plant which went into production in 1973 at Ravenna, Italy.

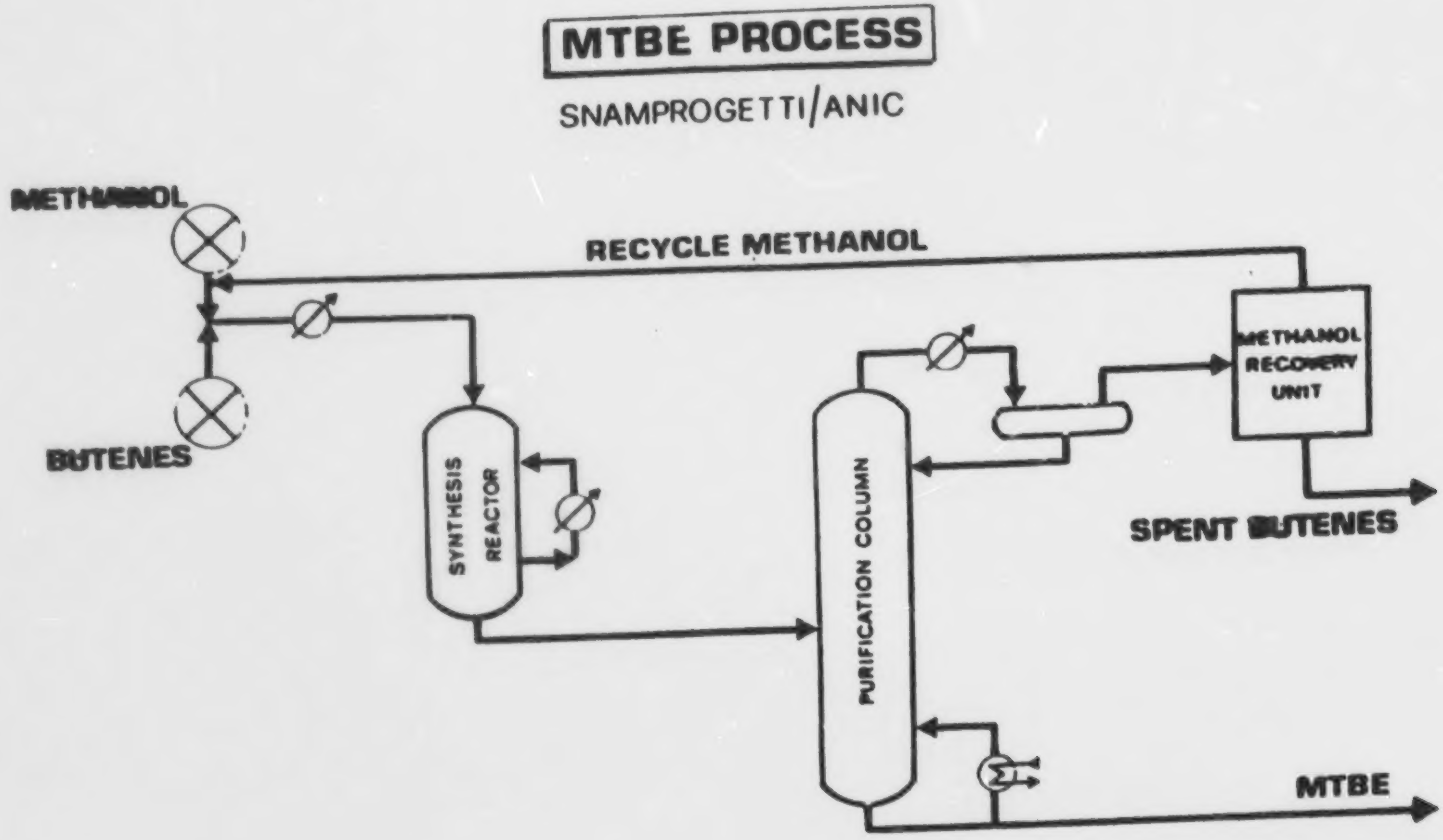

MTBE PROCESS
SNAMPROGETTI/ANIC
METHANOL
RECYCLE METHANOL
BUTENES
SYNTHESIS REACTOR
PURIFICATION COLUMN
METHANOL RECOVERY UNIT
SPENT BUTENES
MTBE

FIG. 3.1 Snamprogetti MTBE Process (Source: 84)

B) MAFKI (HUNGARIAN OIL AND RESEARCH INSTITUTE) PROCESS

Feed: C_4 Stream containing 10 - 50 vol.% of isobutene.

Process: The process flow scheme is shown in Figure 3.2. The unit is made up of the reactor, the washtower (extractor), methanol-water distillation column and MTBE distillation column. Methanol and C_4 stream are mixed, preheated to about 100°C, mixed with a sulfuric acid catalyst stream and fed into the reactor. Excess methanol is used which prevents the polymerization of unsaturated compounds in the reaction mixture. The reactor is internally cooled by a water cooled heat exchanger. The reaction takes place in a homogeneous liquid phase, thereby ensuring uniform catalyst distribution with no sulphonation side reaction.

The reaction product from the reactor on being cooled to 20°C gives two immiscible phases. The sulfuric acid catalyst phase is easily separated and recycled. The hydrocarbon phase is fed to the extractor where methanol is removed by scrubbing with water. NaOH is injected into the wash water in order to neutralize any acid left in the hydrocarbon phase. The methanol-water stream from the extractor bottom is fed to a methanol-water distillation column, where MeOH is recovered from the top of the column and recycled to the reactor. Water from the bottom of the column is recirculated to the extractor. A C_4-MTBE mixture is sent to the MTBE distillation column where a C_4 raffinate is recovered as overhead product while MTBE product of 98% purity is recovered from the bottom of the column. The C_4 raffinate is claimed to contain about 2 vol.% isobutene, less than 10 ppm MeOH and unreacted hydrocarbons (8, 9, 10).

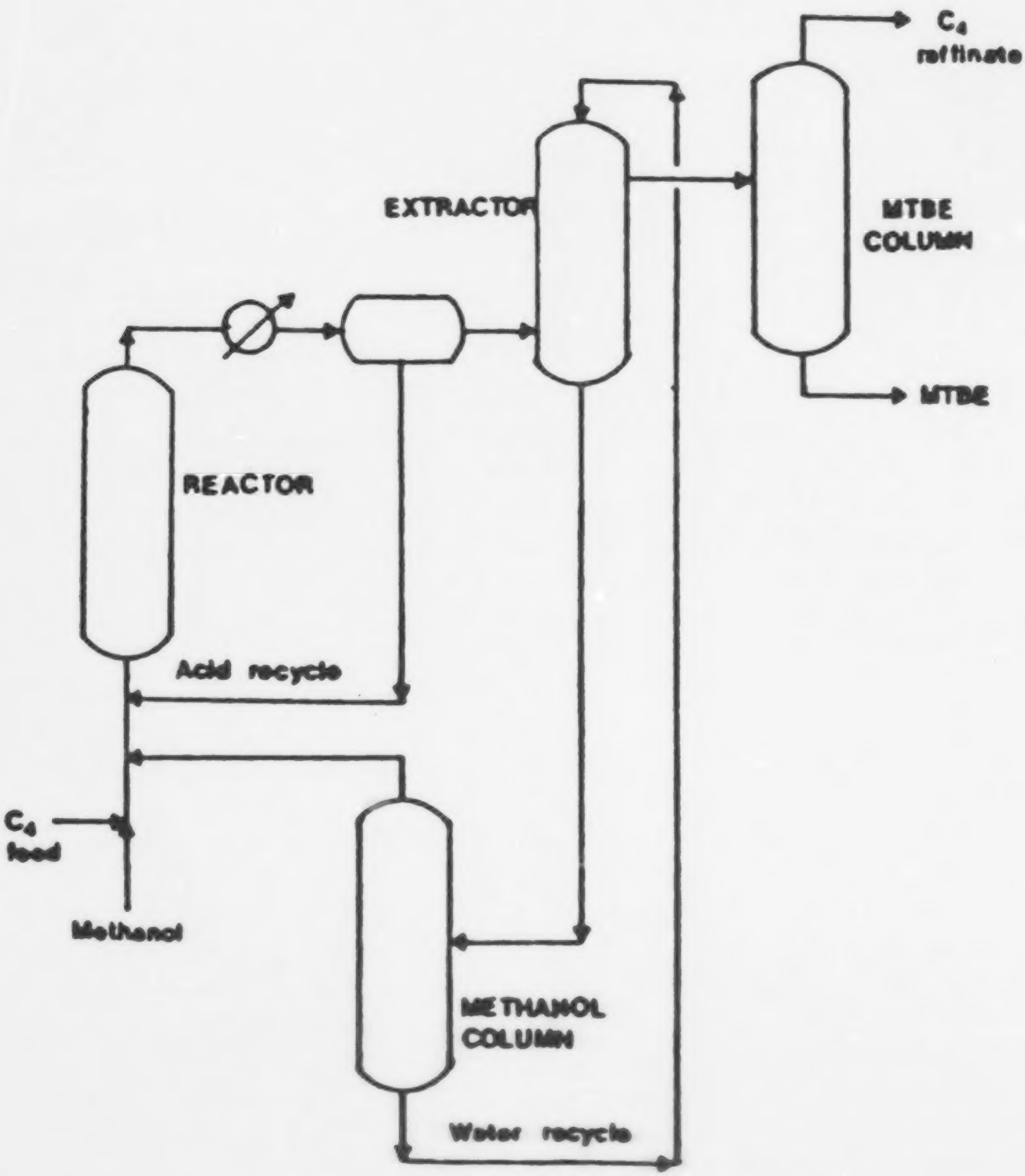

C_4 raffinate
EXTRACTOR
MTBE COLUMN
MTBE
REACTOR
Acid recycle
C_4 feed
Methanol
METHANOL COLUMN
Water recycle

FIG.: 3.2 MAFKI's MTBE Process Flow Diagram (Source: 10)

Reactor: Tubular-tube bundle with internal water cooling.

Catalyst: Sulfuric acid.

C) IFP (INSTITUT FRANCAIS DU PETROLE) PROCESS

Feed: Any C_4 fraction containing isobutylene:

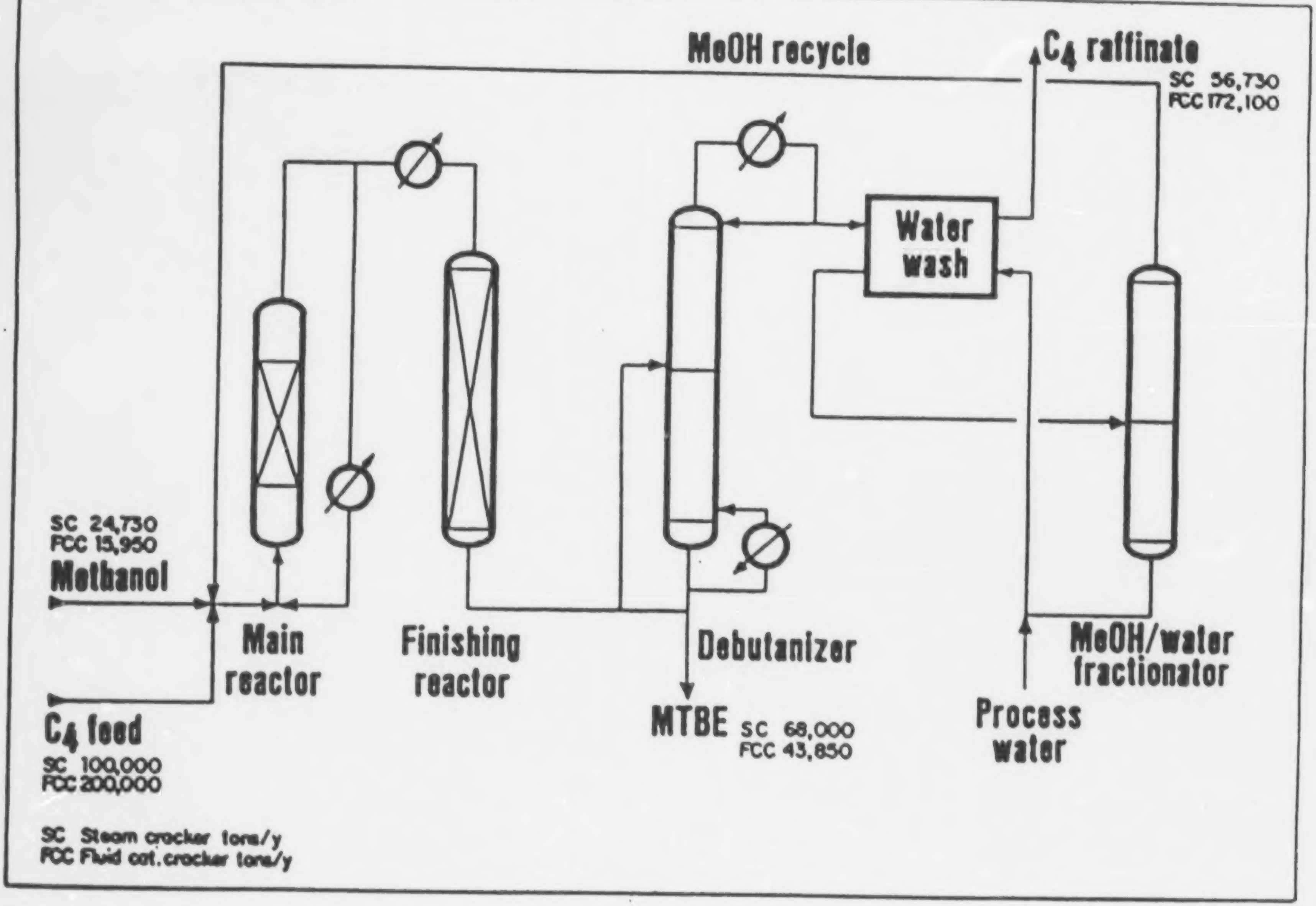
- steam cracker C_4's after butadiene extraction containing about 45 wt% isobutylene
- FCC C_4 cuts at a concentration range of 10-15 wt.% (11).

Process: The IFP process like other MTBE processes is made up of three sections: reaction, fractionation and purification (see Figure 3.3). IFP's process has an original reactor system.

The reaction is performed in the liquid phase at a temperature below 100°C. Two reactors are used. The main reaction occurs in the first reactor which is specially designed for smooth operations. A final conversion level is achieved using a second reactor (finishing reactor) which is operated at a lower temperature.

Reactor: The first reactor, where about 80% of the reaction takes place, is an expanded bed reactor. It is operated in an upflow mode with a 25 - 30% expansion of the catalyst bed. IFP claims the following advantages over conventional reactors (tubular exchange type or fixed-bed downflow) (11,12).

FIG.: 3.3 IFP's MTBE Process (Source: 11)


MeOH recycle
C_4 raffinate
SC 56,730
FCC 172,100
Water wash
SC 24,730
FCC 15,950
Methanol
Main reactor
Finishing reactor
Debutanizer
MTBE SC 68,000
FCC 43,850
MeOH/water fractionator
Process water
C_4 feed
SC 100,000
FCC 200,000
SC Steam cracker tons/y
FCC Fluid cat. cracker tons/y

- inexpensive construction (tubular reactor system is made up of tubes > 1000)
- more efficient transfer of heat from the catalyst particles in motion to the bulk fluid, thereby avoiding overheating of the catalyst particle (extension of catalyst life)
- easy catalyst loading and unloading of the reactor made possible by this chamber type reactor
- little or no pressure drop across the reactor bed, thereby avoiding bed plugging
- possibility of operations at temperatures higher than would be allowed in a fixed-bed system, thereby reducing catalyst consumption.

Catalyst: Acidic ion-exchange resin

Conversion: Isobutene conversion ranges from 98% for one stage reaction scheme, whereas the installation of an additional second stage reactor to process the C_4 overhead raffinate will give a conversion of up to 99.9% (13).

Product: The product MTBE stream includes:

- MTBE (98.5% min. up to 99%+)
- C_4's (0.4% max.)
- MeOH (0.5% max.)
- TBA (0.3% max.)
- Dimers (0.3% max.)

IFP has patented associated technologies to back up the MTBE process some of which include:

- MTBE separation from reaction products (14);
- Conversion of C_4's to gasoline and butane (15);
- Process for producing high octane gasoline from C_3/C_4 olefinic cuts(16);
- Process for removing isobutene from a C_4 cut and producing MTBE (17).

D) CR&L/NEOCHEM's MTBE PROCESS

Feed: Mixed C_4's

Process: This process is entirely different from conventional processes. The feed is water washed in a feed wash column, mixed with MeOH and sent through guard beds (see Figure 3.4a). The guard beds serve a dual purpose: first, as a small adiabatic reaction vessel and second, as a catalyst poison scavenger. The treated mixed feed is then sent through a catalytic distillation unit. This vessel is a reactor and a distillation column, a fusion of two operations. The first is the catalyzed reaction of IB and MeOH to MTBE, and the other is the distilling of the products so as to remove them quickly from the reaction zone (18). The product separation section is similar to that of a conventional unit.

Reactor: The reaction vessel is made up of trays and packed beds. The packed bed has a catalyst support system, consisting of fiberglass cloth imbedded with stainless steel wire mesh. The wire is not only a stiffener, but also acts as a distillation medium. The stacked bales constitute the reactor catalyst bed. Figure 3.4b shows the catalytic distillation column.

Catalyst: Strong-cation exchange resin in granular form (0.25 to 1 mm). The finer catalysts are preferred because they provide a higher surface area, but also result in high pressure drops through the reactor.

Conversion: above 99%.

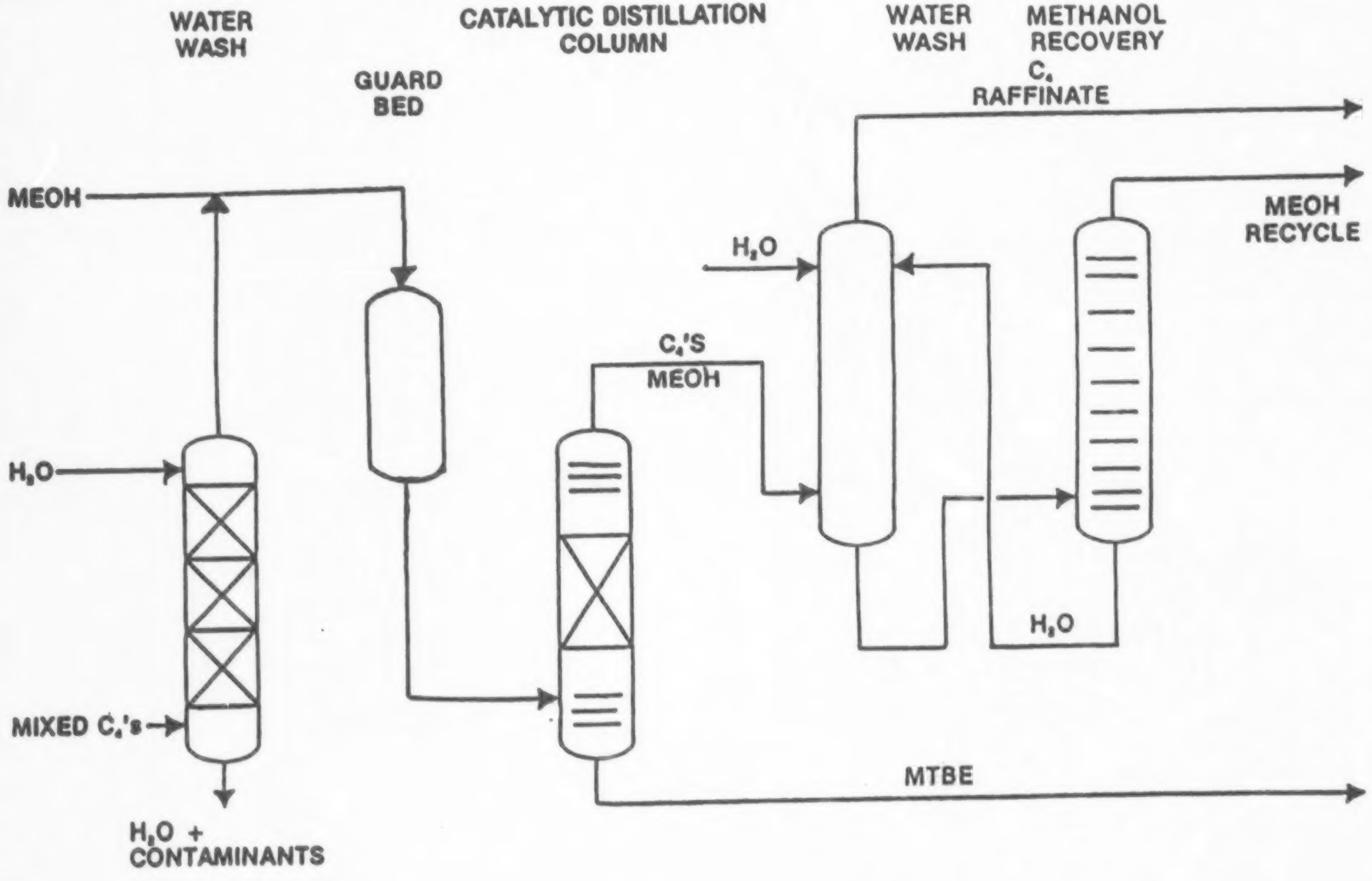

WATER
WASH
CATALYTIC DISTILLATION
COLUMN
WATER
WASH
METHANOL
RECOVERY
GUARD
BED
C_4
RAFFINATE
MEOH
MEOH
RECYCLE
H_2O
C_4'S
MEOH
H_2O
MIXED C_4's
H_2O
MTBE
H_2O +
CONTAMINANTS

FIG.: 3.4 (a) CR&L/NEOCHEM MTBE PROCESS (Source: 19)

Chemical Research and Licensing/NEOCHEM claims the following advantages of its technology over all other MTBE technologies (19,20):

- combined reaction and distillation in a single column, thereby reducing equipment requirements
- maximum conversion of isobutylene and formation of MTBE
- low operating costs due to efficient utilization of the heat of reaction
- product removal as it is formed allows operation at higher temperature than in conventional units
- the reactor configuration has the following advantages (19):
  - o reduced fines generation
  - o extended catalyst life by elimination of hot spots
  - o elimination of high concentration MTBE zones
  - o insignificant corrosion problems due to eliminating catalyst contact with the vessel

CR&L has patented technologies related to this process. More than 15 patents have been issued in the USA and more than ten have been filed in Canada.

Over the years a lot of processes and related technolgies for MTBE synthesis/production have been patented. Some of these patented processes are summarized in Table 3.1 (adapted from 10). Table 3.2 shows a list of MTBE process licensors and their respective process characteristics (adapted from 10).

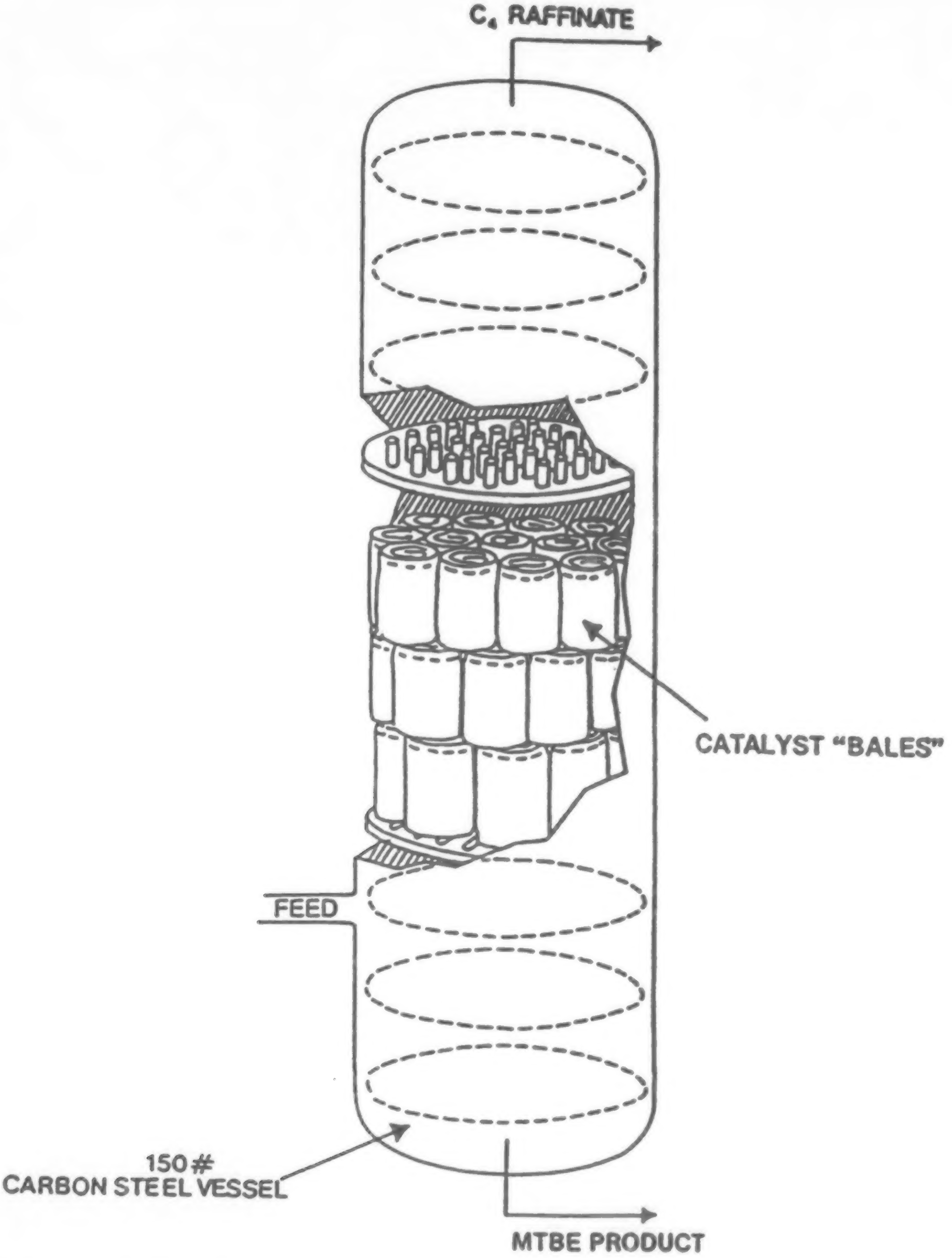

C₄ RAFFINATE
CATALYST "BALES"
FEED
150#
CARBON STEEL VESSEL
MTBE PRODUCT

FIG.: 3.4(b) CR&L/NEOCHEM CATALYTIC DISTILLATION TOWER (Source: 19)

TABLE 3.1 OVERVIEW OF SELECTED PATENTS ON MTBE SYNTHESIS (IB = ISOBUTENE)
(Adapted from 10)

Page 1

Assignee	Date	Feed	Catalyst	Reaction Conditions	Results	Ref.
Leum, L.N. et al Atlantic Refinery Co.	6-09-49	MeOH/IB = 1.1/1	Acidic Ion Exchange Resin	210-250^{o}F liquid phase 1.1 lb olefin/lb catalyst/hr	77% yield	(20)
Verdol, J.A. Sinclair Research	11-02-64	C_4(51.5 wt% IB) MeOH/IB = 4.51/1	Acidic Ion Exchange Resin	160^{o}F, liquid phase, LHSV = 12	85% yield	(21)
Brown R.W. et al Sun Oil	5-11-74	FCC C_4 (5-20 wt% IB) MeOH/IB = 1.5/1	Acidic Ion Exchange Resin	180^{o}F, liquid phase, 25 lb feed/lb catalyst/hr	85% conversion of IB	(22)
Ancillotti F. et al Snamprogetti	27-11-75 7-09-76	C_4 (50 wt.% IB) MeOH/IB = 1/1 in 1st stage and 4/1 in 2nd stage	Acidic Ion Exchange Resin	50-60^{o}C liquid phase, LHSV = 5 in each stage	99% conversion 98% selectivity on IB	(23) (24)
Texaco Dev. Corp.	28-05-76	FCC C_4 (11% wt% IB) MeOH/IB = 2/1	Acidic Ion Exchange Resin	93^{o}C, Liquid phase, 2 lb IB/lb catalyst/hr	97% selectivity on IB	(25)
Auclair P. et al, Enterprise de Recherches et d'Activites Petrolieres	24-12-76	C_4 hydrocarbon mixture	Acidic Ion Exchange Resin	60^{-150o}C, 40-60 bars, LHSV = 4 to 20	76-81% conversion on IB, 97-99% selectivity no butane conversion	(26)
Wanatabe Y. et al Sumitomo Chemical Co.	27-01-77	31.4 g MeOH 56.6g C_4 mixture	0.5g 97% H_2SO_4	110^{o}, liquid phase, 90 min, batch reaction	36% MeOH conversion	(27)

TABLE 3.1 OVERVIEW OF SELECTED PATENTS ON MTBE SYNTHESIS
(Adapted from 10)

Page 2

Assignee	Date	Feed	Catalyst	Reaction Conditions	Results	Ref.
Herbstman S. et al Texaco Dev. Corp.	4-01-77	MeOH, IB from butane isomerization and dehydrogenation	Amberlyst 15 Ion Exchange Resin	$93^{o}C$, 21 kg/cm^2 liquid phase	--	(28)
Steinmetz I. Sun Oil Co.	10-05-77	C_4 (11% IB) MeOH/IB = 0.55/1	Amberlyst 15 Ion Exchange Resin	$160-200^{o}F$, 30-300 psig, $180^{o}F$, 200 psig	55% conversion on IB	(29)
Laky J. et al Hungarian Oil & Gas Research Institute (MAFKI)	12-05-77	C_4 (25% IB)	20% H_2SO_4	$50-120^{o}C$, liquid phase $90^{o}C$, 20 atm.	93-98% conversion on isobutene	(30)
Ancillotti F. et al Snamprogetti	2-08-77	Steamcracker C_4 MeOH/IB = 1/1	Acidic Ion Exchange Resin	$60-80^{o}C$, liquid phase LHSV = 5-35	75-80% conversion on IB	(31)
Guttmann A.T. et al Standard Oil, Ohio	17-10-77	MeOH and IB mixture	$H_4SiMo_{12}O_{40}$ $x H_2O$	$135^{o}C$, liquid phase	100% MTBE selectivity	(32)
Huels A.G.	2-01-78	Cracked C_4 (45 wt% IB) MeOH/IB = 1.1/1 to 1.4/1	Acidic Ion Exchange Resin	$40-80^{o}C$, liquid phase LHSV = 0.7 to 2.6	96-98.5% conversion of IB, 99% selectivity	(33)
Obenaus F. et al Huels A.G.	5-01-78	MeOH/IB = 2/1	Acidic Ion Exchange Resin	$80^{o}C$, liquid phase	80.8% yield	(34)

TABLE 3.1 OVERVIEW OF SELECTED PATENTS ON MTBE SYNTHESIS
(Adapted from 10)

Assignee	**Date**	**Feed**	**Catalyst**	**Reaction Conditions**	**Results**	**Ref.**
Ancillotti F. et al Snamprogetti	31-01-78	MeOH/IB = 0.4 in 1st stage and 1.5 in 2nd stage	Acidic Ion Exchange Resin	60-70^{o}C, liquid phase LHSV = 5 in 1st stage, LHSV = 20-50 in 2nd stage	98% conversion 98-99% selectivity on IB	(35)
BASF	12-04-78	Cracked C_4 (46 wt% IB) MeOH/IB = 1/1	Acid Ion Exchange Resin	50-120^{o}C, liquid phase 0.1 to 1 hr residence time, catalyst suspended in liquid	75-80% conversion 99% selectivity	(36)
Brunner E. et al BASF	20-04-78	MeOH, IB	Acidic Ion Exchange Resin	80^{o}C, 11.5 bars, liquid phase	99% conversion on IB 99% selectivity	(37)
BASF	8-09-78	C_4 (50 wt% IB) MeOH/IB = 1/1 in 1st stage and 2/1 in 2nd stage	Acidic Ion Exchange Resin	40-90^{o}C, 11.5 bars, liquid phase	99% conversion on IB 99% selectivity	(38)
Deutsche Texaco	15-09-78	Cracked C_4 (22 wt% IB) MeOH/IB = 0.9/1 in 1st stage	Strong acidic Ion Exchange resin in 1st stage, less acidic resin in 2nd stage	70^{o}C, liquid phase LHSV = 4 in 1st stage LHSV = 2 in 2nd stage	99% conversion on IB Very small conversion of butadiene	(39)
Izumi Y. Tokuyama Soda Co.	3-02-79	79g MeOH 37g IB	1.0g silico-tungstic acid	100^{o}C, liquid phase, 1 hr batch reaction	39.4g MTBE	(40)

TABLE 3.1 OVERVIEW OF SELECTED PATENTS ON MTBE SYNTHESIS
(Adapted from 10)

Page 4

Assignee	Date	Feed	Catalyst	Reaction Conditions	Results	Ref.
Izumi Y. et al Tokuyama Soda Co.	2-05-79	MeOH/IB = 1/1	Solid acid catalyst prepared from Na_2WO_4, $ZrOCl_2$ and HCl	120°C, gas phase, GHSV = 2000	10% MeOH conversion	(41)
Kiewlicz W. et al Polish Science Academy	31-05-79	MeOH/IB	Solid acid catalyst H_2SO_4, H_3PO_4 on Al_2O_3, SiO_2 or Aluminum silicate support	100°C, gas phase	--	(42)
Takezono T. et al Nippon Oil Co.	8-01-80	MeOH/IB = 0.6 to 1.4	Acidic Ion Exchange Resin	0-100°C, 1-5 atm, liquid phase, LHSV = 0.1 TO 50	--	(43)
Smith, Jr. L.A. et al CR&L	19-03-80	FCC C_4 MeOH/IB = 1.1/1	Amberlyst 15 Ion Exchange Catalyst	150-200°F, liquid phase, 10-15 lb feed/lb catalyst/hr simultaneous etherification and distillation	96% isobutene conversion, 98.4% selectivity	(44)
Torck B. et al IFP	22-05-80	Steamcracker C_4 or FCC C_4	Amberlyst 15 Ion Exchange Catalyst	One fixed bed, one ebullating (dispersed) bed	92-98% IB conversion	(45) (46)
Oyama K. et al Toyo Soda Manufac. Co.	11-11-81	MeOH and IB	Perfluorcarbon polymers with sulfonic acid groups eg. Dupont's Nafion	Liquid phase reaction at 30-150°C and 2-80 atm. Catalyst can be suspended in the liquid or in a fixed bed reactor	82.1% conversion of MeOH 99.7% selectivity to MTBE	(47)

TABLE 3.1 OVERVIEW OF SELECTED PATENTS ON MTBE SYNTHESIS
(Adapted from 10)

Page 5

Assignee	**Date**	**Feed**	**Catalyst**	**Reaction Conditions**	**Results**	**Ref.**
Daniels J.A. et al Imperial Chem. Ind.	30-06-82	MeOH and IB MeOH/IB = 2.4	Zeolite with SiO_2/Al_2O_3 10	90°C for 1 hr in an autoclave for liquid phase reaction. Tubular reactor for gas phase 1-100 bars	92.3% conversion on IB 98% selectivity to MTBE	(48)
Fujiwara Y. et al Nippon Oil Co.	13-09-83	C_4 mixture MeOH/IB = 0.75 to 1.2	Amberlyst 15 Ion Exchange Resin	65-85°C in 1st reactor, 30-50°C in 2nd reactor, 5-30 atm., LHSV = 0.5 to 15	96% conversion on IB	(49)
Briggs, B.A. UPO Inc.	01-11-83	MeOH and IB MeOH/IB = 1.1/1 to 1.5/1	Ion Exchange Resin	5o-100°C below 200 psig pressure. Liquid phase reaction, etherification and fractionation.	99% IB conversion	(50)
Hanes R.M. National Distillers and Chem. Corp.	29-11-83	MeOH and IB MeOH/IB = 0.5/1 to 1/1	Heterogeneous Inorganic Catalyst from Boron phosphate, Blue Tungsten oxide and Alumino silicate zeolite.	125°C to 200°C at a pressure of 25-1000 psig. Autoclave stirred or fixed bed reactor.	Selectivity to MTBE can be as high as 99.8%	(51)
Rothschild W.G. Diamond Shamrock	14-03-84	IB containing Hydrocarbon and MeOH MeOH/IB = 1.2/1	Strong Acid Cation Exchange Resin	70°C in a batch stirred tank reactor.	96% conversion to MTBE	(52)

TABLE 3.1 OVERVIEW OF SELECTED PATENTS ON MTBE SYNTHESIS
(Adapted from 10)

Page 6

Assignee	Date	Feed	Catalyst	Reaction Conditions	Results	Ref.
Schleppinghoff B. et al EC Erdoelchemie	5-03-85	MeOH and IB MeOH/IB = 1/1	Acid Cation Exchange Resin	40-90^{0}c at a pressure of 3-20 bars. WHSV = 1 to 5, liquid phase in two fixed bed reactors	99 wt% IB conversion	(53)
Groeneveld C.R. et al	19-11-85	C_4 Raffinate II and MeOH	Strong Acid Cation Exchange Resin	Isomerization and etherification	Full conversion of IB to MTBE	(54)

TABLE 3.2 MTBE PROCESS LICENSORS (Adapted from 10)
(IB = isobutene)

Page 1

Licensor	**Feedstock**	**Catalyst**	**Process Characteristics**	**Ref.**
ARCO	MeOH, IB from steamcracker or Butane from NG	Ion Exchange Resin	Isomerization on n-butane followed by dehydrogenation, fixed-bed, liquid phase, distillation, high conversion, low capital investment, high selectivity	(55) (78) (80)
CR&L/Neochem	MeOH, IB from FCC	Ion Exchange Resin	Catalytic Distillation - simultaneous reaction and distillation in a single reactor, low energy comsumption, high conversion	(56) (57) (15) (58)
Davy International	MeOH, IB from normal Butane	Ion Exchange Resin	Butane Isomerization, debutanization and dehydrogenation, etherification in a fixed bed, large scale production	(59).
ED Erdol Chemie GmbH	MeOH, IB (5-60 wt%) containing hydrocarbons	Ion Exchange Resin	Two-staged simple shaft furnace type reactors, high conversion, low energy consumption, methanol recovery by adsorption	(60) (61) (62) (63)
Gulf Canada	MeOH, IB from FCC or steamcracker	Ion Exchange Resin	One or two fixed beds, liquid phase distillation	(64) (65) (66)
Huls AG	MeOH, natural gas condensate containing n-butane or isobutane	Ion Exchange Resin	Isomerization of n-butane, dehydrogenation of isobutane, etherification in two fixed beds, liquid phase, distillation, three process variations depending on required product purity	(67) (68) (69) (70)

TABLE 3.2 MTBE PROCESS LICENSORS (Adapted from 10)
(IB = Isobutene)

Page 2

Licensor	Feedstock	Catalyst	Process Characteristics	Ref.
Institut Francais du Petrole (IFP)	MeOH, IB from FCC or steamcracker	Ion Exchange Resin	Two ebullating bed reactors, liquid phase, distillation	(11),(12) (71),(72)
Nippon	MeOH, IB from FCC or steamcracker	Strong Acid Cation Exchange Resin	Three fixed bed reactors followed by distillation. Third reactor is filled with a water insoluble solid particulate acid neutralizing agent	(49)
MAFKI	MeOH, IB (10-50 wt%) continaing C_4 fractions	Sulfuric Acid	Single reactor, homogeneous liquid phase, liquid extraction, distillation, high conversion	(8) (9)
Petroflex	MeOH, IB	Ion Exchange Resin	Etherification	(10)
Phillips Petroleum	MeOH, IB	Ion Exchange Resin	Contacting the IB feed with an acid solution (H_2SO_4) prior to contacting the catalyst with the feed, dual reactor, distillation, water wash, drying. Low investment, low utility requirements, very little by-product formation, unreacted olefins may be fed to alkylation without further treatment	(73)
Shell International Research B.V.	MeOH, IB from C_4 streams	Ion Exchange Resin	Etherification	(74)
Snamprogetti/ANIC	MeOH, IB from FCC or steamcracker C_4 stream	Ion Exchange Resin	One or two fixed bed reactors depending on required product purity, liquid phase, distillation	(1),(2),(3) (4),(6),(75)

TABLE 3.2 MTBE PROCESS LICENSORS (Adapted from 10)
(IB = Isobutene)

Page 3

Licensor	**Feedstock**	**Catalyst**	**Process Characteristics**	**Ref.**
Sumitomo Chemical Co.	MeOH, spent butanes containing IB	Ion Exchange Resin	High yield, good for butanes separation	(79)
Sun Oil	MeOH, IB from FCC	Ion Exchange Resin	Fixed bed, liquid phase, distillation, recycle MeOH extracted by water wash	(10)
Deutsche TEXACO	MeOH, IB from FCC	Ion Exchange Resin	Two fixed beds, excess MeOH is extracted by water from reactor product, distillation, high conversion	(76) (39)
BP (Etherol Process for MTBE)	MeOH, IB from FCC	Ion Exchange Resin	Dual reactor system, fixed bed, liquid phase, distillation and adsorption/desorption for MeOH separation	(77)

3.1.2 Integrated Technologies for Processing C_4's

These technologies are based on fitting together some of the following processes. (The goodness of fit is determined by the overall process economics.)

- hydrogenation
- etherification
- oligomerization
- solvent extraction
- dimerization
- polymerization
- hydration
- alkylation
- fractionation/distillation

The product slate varies from oxygenates to petrochemical intermediates. Noteworthy in this group of technologies are commercially proven integrated systems developed by the following companies:

- Huels A.G., Marl, West Germany (81)(82)
- Sumitomo Chemical Ltd., Osaka, Japan (83)
- Snamprogetti, Milan, Italy (84)
- Krupp-Koppers GmbH, Essen, West Germany (85)

1. HUELS A.G., MARL, WEST GERMANY (81)(82)

Process: Huels A.G. developed an integrated system of individual C_4 processes which were fitted to each other in such a way that proper and economic use of all of the components of the C_4 fraction was affected. Typical and worthy of special mention are two specific processes.

a. **The Huels TBA Process (Tertiary Butyl Alcohol)**

Isobutylene contained in mixed butylenes (generally known as raffinate-1) and water plus a recycle stream (a recycle stream containing TBA) are fed into a reactor packed with non-corrosive cation exchange resin. The reaction products go through three separation stages. Spent C_4-HC from the top of the first tower is generally blended into the gasoline pool in refineries. From the bottom of the tower, raw TBA/water product is drawn or sent to a second tower for further separation. In this second tower, dimerized C_8 olefins are taken out from the top, whereas TBA/water goes out of the bottom. In a third tower, this bottom mixture is separated into a spent water stream and TBA/water azeotrope product. The water is free of hydrocarbons and can be disposed of or recycled. See Figure 3.5.

b. **The Huels Octol Process**

N-butenes are oligomerized to a mixture of highly branched C_8, C_{12}, and C_{12+} olefins in the presence of a solid acid catalyst at higher temperatures.

Note that the first stage in any of these two processes is the hydroisomerization of butene-1 to butene-2. One can then separate the mixture by distillation into an isobutane and a butene rich stream. The isobutene rich stream is well suited to the production of TBA while the butene rich stream is good for the manufacture of butene oligomers, mainly octenes.

Plant: The above two Huels processes were integrated for TBA/Di-n-butenes production at General Sekiyu Refineries in Sakai, Japan, for the first time. A 50,000 t/yr TBA and a 45,000 t/yr octene plant went on stream in 1986.

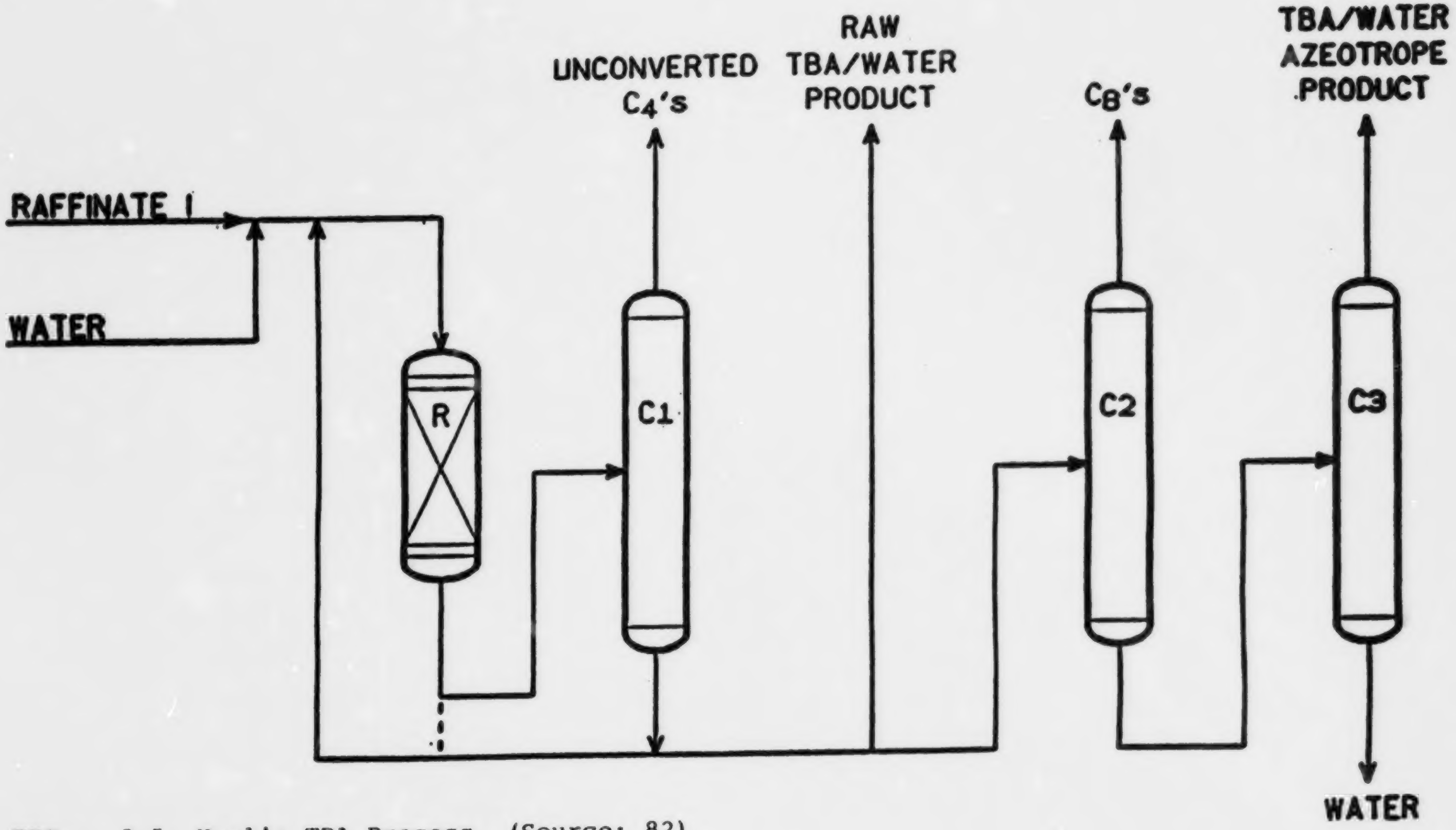

UNCONVERTED
C_4's
RAW
TBA/WATER
PRODUCT
C_8's
TBA/WATER
AZEOTROPE
PRODUCT
RAFFINATE I
WATER
R
C1
C2
C3
WATER

FIG.: 3.5 Huel's TBA Process (Source: 82)

2. SUMITOMO CHEMICAL COMPANY LTD., OSAKA, JAPAN (83)

Sumitomo engineers, in their bid to solve their C_4 problems developed a process to separate isobutene and butene-1 from spent C_4 fraction (raffinate-1).

Basis: Table 3.3 below (taken from (83) shows the typical composition and physical properties of raffinate-1.

TABLE 3.3 RAFFINATE-1 STREAM PROPERTIES

	Content wt%	Boiling Point °C	Melting Point °C	SG at 15°C
Isobutane	3.7	-11.7	-159.6	0.56
Isobutene	43.9	-6.9	-140.3	0.60
1-Butene	27.8	-6.3	-183.4	0.60
n-Butane	11.6	-0.5	-138.4	0.58
t-2-Butene	8.2	0.9	-105.5	0.61
c-2-Butene	3.7	3.7	-139.2	0.63
1,3-Butadiene	0.8	-4.4	-108.9	0.62
Others	0.3			

The table above illustrates that:

- distillation would be unsuitable for the separation of isobutene and 1-butene because their boiling points are almost the same.

- once isobutene and 1-butene are separated, other components can easily be separated by distillation.

Process: Sumitomo's MTBE process is based on the selective reaction of isobutene in raffinate-1 with methanol in the presence of an ion exchange resin catalyst. The MTBE, after separation through distillation, is cracked with a solid acid catalyst to isobutylene and methanol. The methanol is returned to the MTBE synthesis loop. For the remaining spent C_4's (raffinate-2), the dienes and acetylenes are selectively hydrogenated and distilled to obtain 1-butene.

In the MTBE cracking step, which is endothermic, a multitubular type reactor is used and all the necessary heat is supplied from outside. An acid catalyst developed by Sumitomo is used. This gas phase reaction takes place at a strictly controlled reaction temperature between 200 and 250°C and a pressure of over 5 kg/cm^2.

For the selective hydrogenation step, Sumitomo uses an in-house modified Palladium catalyst which completely hydrogenates dienes and acetylenes, as well as minimizes the isomerization of 1-butene to 2-butene. Figure 3.6 shows the flow scheme for this process.

Plant: Sumitomo Chemical Company Ltd. put a plant on stream using their MTBE process at its Chiba Works, Chiba, Japan, in 1984. The plant is reported to be operating well and has a capacity of 50,000 t/yr in total production of isobutene and butene-1.

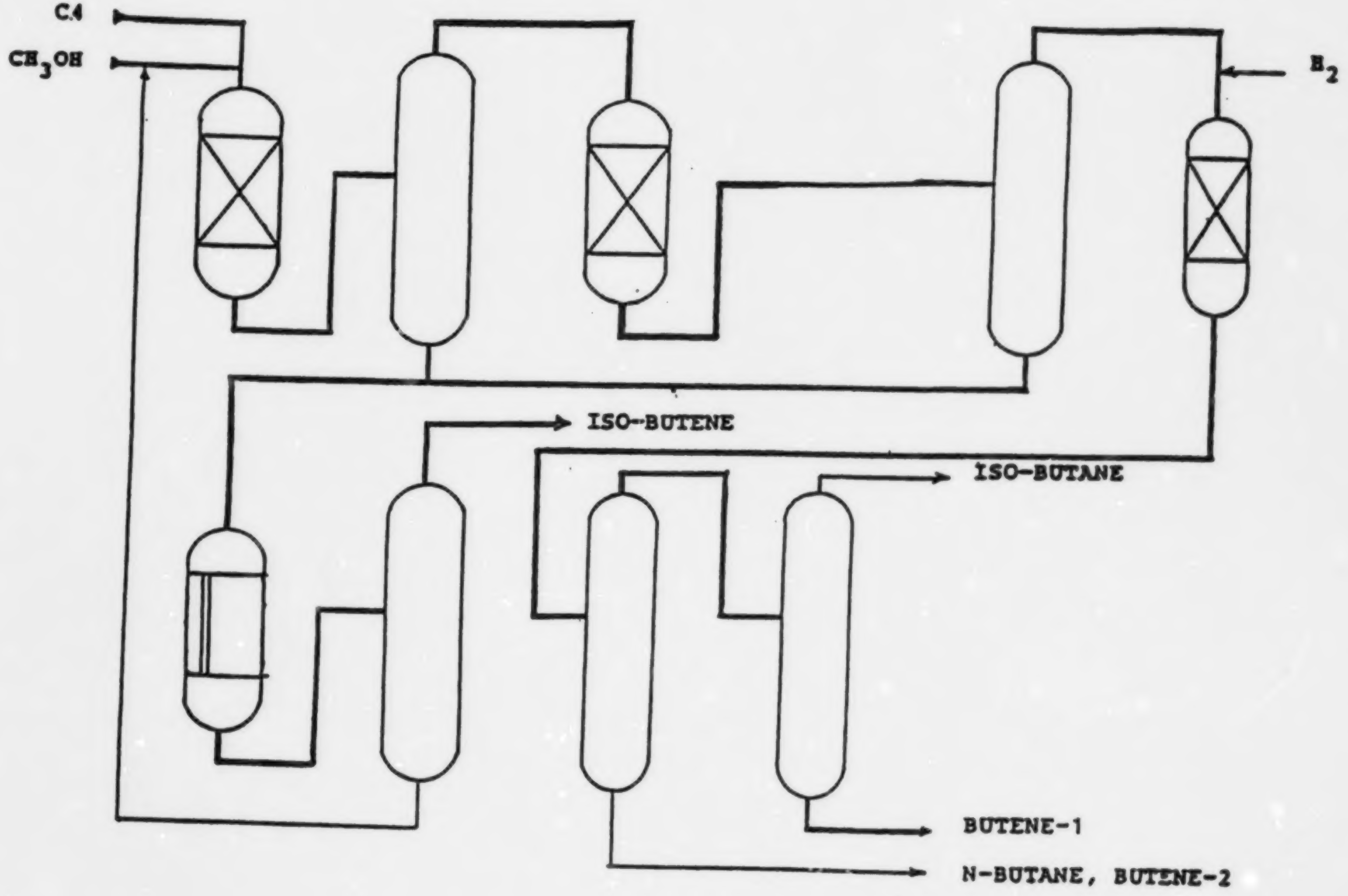

C4
CH_3OH
H_2
ISO-BUTENE
ISO-BUTANE
BUTENE-1
N-BUTANE, BUTENE-2

FIG.: 3.6 Sumitomo's Process for C_4 Separation (Source: 83)

3. SNAMPROGETTI, MILAN ITALY

Snamprogetti has two processes which, when integrated, transform the C_4's into saleable products.

Feed: Snamprogetti claims that feed can be any C_4 stream with some isobutene content as follows:

- C_4's from steam cracking (18 to 32 wt% before butadiene extraction and 40 to 50 wt% after butadiene extraction)

- C_4 cuts from FCC units (10 to 20 wt% isobutene)

- field butanes (40 to 60 wt% after dehydrogenation)

Process: The production of high purity isobutene requires two integrated Snamprogetti processes:

a. Snamprogetti/ANIC MTBE Synthesis Process

The C_4 feed and methanol are passed through an MTBE snythesis reaction loop, where, under mild temperature conditions, MTBE synthesis takes place. The reactor product stream is then fractionated in the MTBE fractionation tower. From the bottom of the tower, MTBE, which is free of both C_4 hydrocarbons and methanol, is recovered. This MTBE is suitable for use as an octane booster in a gasoline pool.

The tower overhead, which is a mixture of unconverted isobutene, C_4 hydrocarbons and azeotropic excess methanol, is sent into another tower where methanol is removed by counter current washing of the stream with methanol free water. Methanol is recovered by fractionation and recycled. Methanol free C_4 raffinate (raffinate-2) is further processed.

b. Snamprogetti MTBE Decomposition Process

MTBE recovered from the MTBE fractionation tower as a side stream is vapourized and passed through an MTBE decomposition reactor. In this reactor, MTBE is converted into pure isobutene and methanol.

The decomposition reactor is a bundle type reactor with catalyst housed within the tubes. The reaction is endothermic and strict control of the reaction temperature is necessary to avoid any condensation phenomena on the catalyst bed.

The reactor products enter an isobutene fractionation tower. The tower bottom stream is recycled to the MTBE synthesis reaction loop. The fractionator overheads are sent into a counter current water wash tower where the methanol-water mixture is removed and fed to a methanol-water fractionation tower common to the MTBE synthesis unit, for methanol recovery. The isobutene product is fractionated. The fractionation tower overhead consists of a small amount of isobutene and DME (dimethylether) which are recycled to the MTBE synthesis loop. The fractionator bottom is the high purity isobutene product.

The catalyst is Snamprogetti developed and is reported to be sufficiently active and highly selective, with respect to the recovery of both isobutene and methanol. Catalyst activity decreases with time and MTBE conversion is kept constant by increasing the operating temperature from an initial value of 180°C to a final value of 270°C. The catalyst life exceeds 8000 hours of continuous operation and the catalyst is regenerable. MTBE conversion is 70 to 80%

per pass, while selectivity to isobutene is 99.5%. The high purity isobutene is said to be as clean and as colourless as water. Pure isobutene is used for the manufacture of the following:

- TBA (tertiary butyl-alcohol)
- DIB (Di-Isobutylene) for C_9 oxo-alcohol and octyl-phenols used as detergent precursors
- DIB and TIB (tri-isobutylene) can be put back into the motor gasoline pool.
- Butyl rubber (copolymerization of isobutene with isoprene; tire inner tubes are made of butyl rubber).

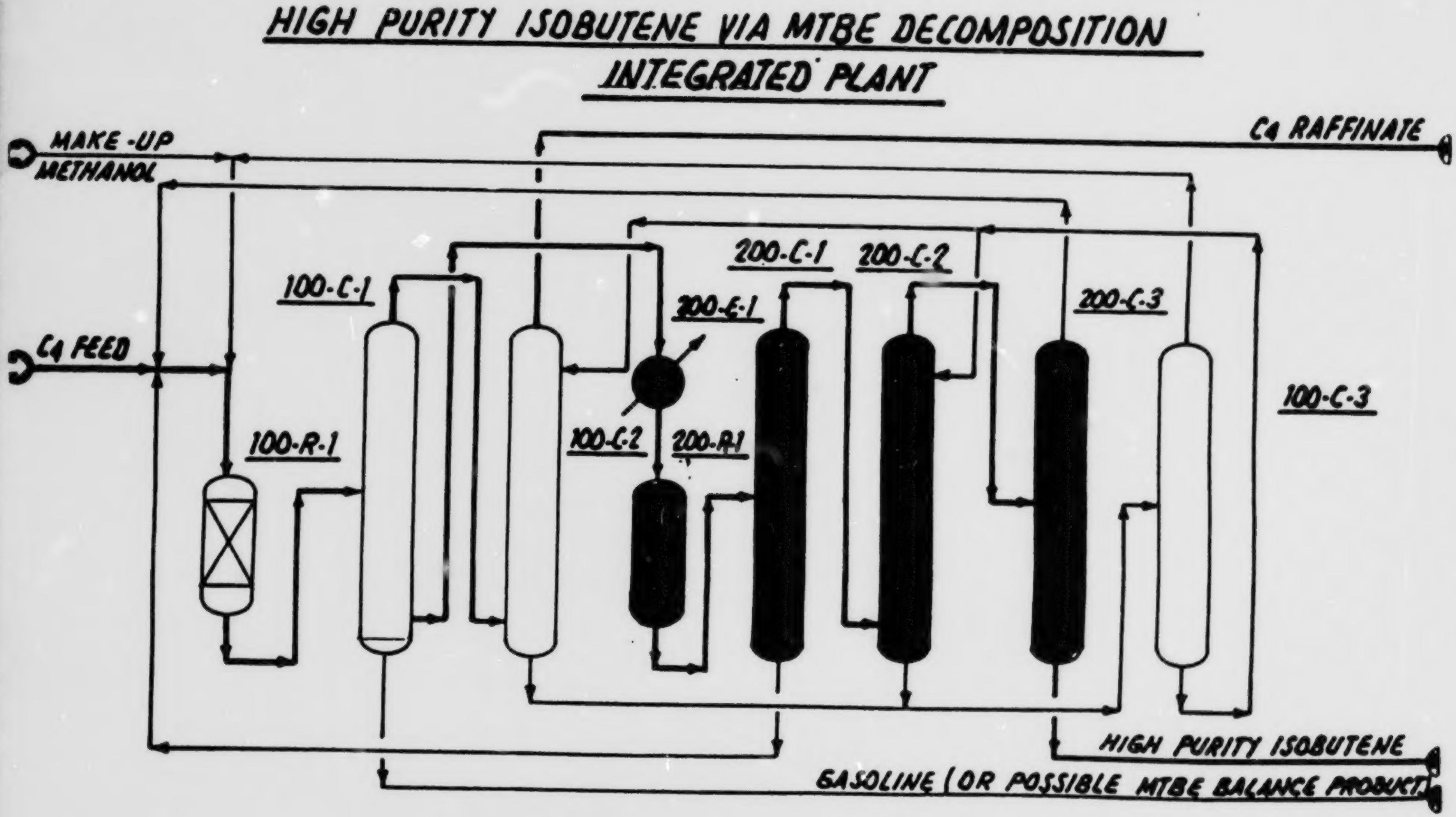

HIGH PURITY ISOBUTENE VIA MTBE DECOMPOSITION
INTEGRATED PLANT
MAKE-UP METHANOL
C4 RAFFINATE
C4 FEED
100-C-1
100-R-1
200-E-1
100-C-2
200-R1
200-C-1
200-C-2
200-C-3
100-C-3
HIGH PURITY ISOBUTENE
GASOLINE (OR POSSIBLE MTBE BALANCE PRODUCT)

FIG.: 3.7 Snamprogetti's Integrated Process (Source: 84)

Plant: Figure 3.7 shows an integrated plant based on Snamprogetti's two processes. A commercial unit was commissioned in Hungary (August 1987). Its capacity is 500 MTP/yr and it uses steam cracking feedstock before butadiene extraction.

4. KRUPP-KOPPERS GMBH ESSEN, WEST GERMANY (85)

Process: The process is based on an efficient separation of butene-1 and butene-2 using extractive distillation. GKT developed a solvent (a solvent mixture from the morpholine group) which is selective in the separation of residual butenes from the butanes. The new solvent was able to adjust the vapour pressure of the C_4 hydrocarbons such that separation by an extractive distillation process became possible -- the Butenex Process. In other words, the vapour pressure curves of the butenes and butanes diverge considerably, facilitating separation by distillation.

With a proper configuration, this process can aid a producer to manufacture an entire range of products.

Plant: Krupp-Koppers built a plant with a capacity of 44,000 metric tons per year of C_4 hydrocarbon mixture. Figure 3.8 illustrates the flow scheme of the plant showing a production of an entire range of C_4 feedstocks. The C_4 cut is also completely utilized.

5. OTHER PROCESSES

Outside of above mentioned processes, there are many other commercially proven processes worth mentioning.

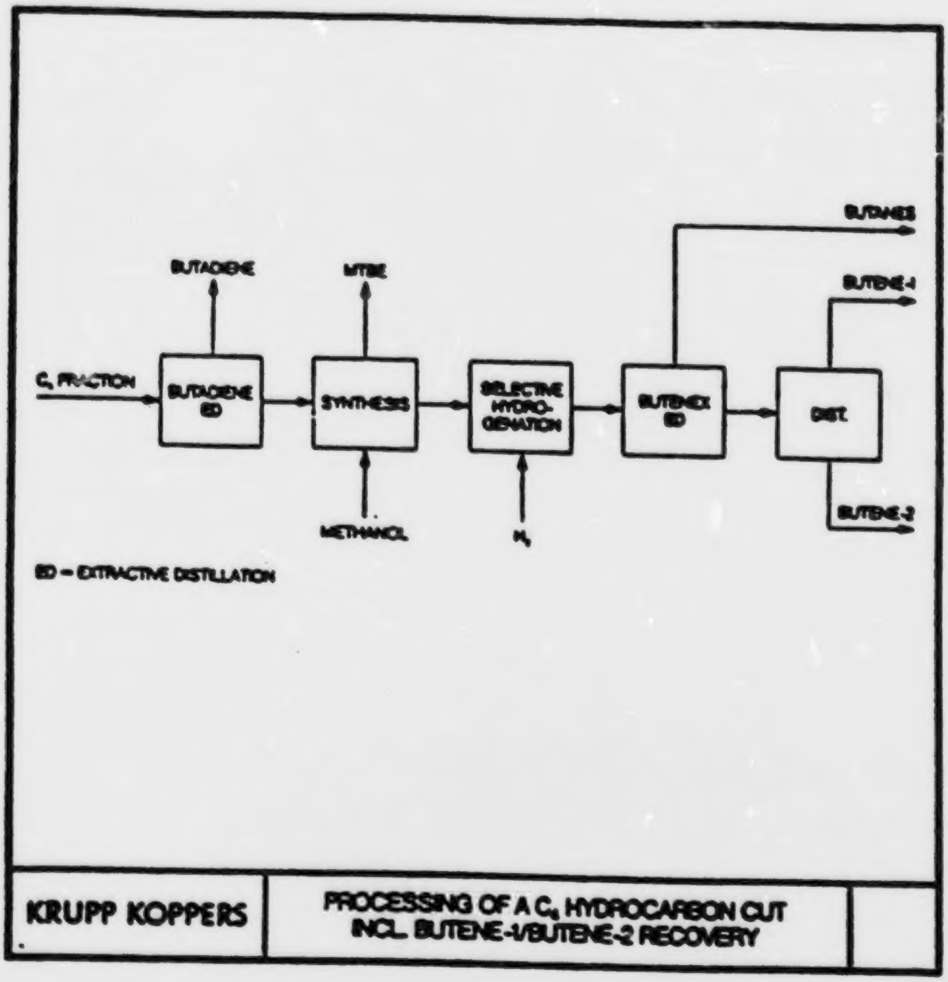

BUTADIENE
MTBE
BUTANES
BUTENE-1
C_4 FRACTION
BUTADIENE ED
SYNTHESIS
SELECTIVE HYDRO-GENATION
BUTENEX ED
DIST.
BUTENE-2
METHANOL
H_2
ED – EXTRACTIVE DISTILLATION
KRUPP KOPPERS
PROCESSING OF A C_4 HYDROCARBON CUT
INCL. BUTENE-1/BUTENE-2 RECOVERY

FIG.: 3.8 Krupp-Kopper's Integrated Plant (Source: 85)

a. Mitsubishi Rayon's Methyl Methacrylate (MMA) Process

Feed is spent butylene-isobutylene after butadiene extraction (raffinate-1). Isobutylene in raffinate-1 is converted to tertiary butyl alcohol (TBA). TBA is separated and oxidized to MMA (methyl-methacrylate).

b. Air Product/Houdry Catofin Process

Feed is light paraffins -- propane, butanes and pentanes. The process claims to convert the light paraffins to a variety of motor fuels. It is an adiabatic, fixed bed dehyrogenation process. Possible variants include:

- "Catofin" based isobutane to GTBA
- "Catofin" based isobutane to MTBE.

c. EC Erdolchemie/BP Etherification Processes

Three processes were developed and comercialized by EC Erdolchemie and BP for the production of high octane methyl ethers from olefinic feedstocks:

i) EC Erdolchemie MTBE Process - MTBE from isobutylene. A unit was commissioned by EC Erdolchemie, Dormagen, West Germany in 1982.

ii) EC Erdolchemie TAME Gasoline Process - TAME gasoline from C_5 cracked naphtha cuts. A 45BPSD EC Erdolchemie unit was commissioned in January 1986. Another unit for Lindsey Oil, U.K., has been completed (5,500 BPSD).

iii) BP Cracked Naphtha Etherification Process - Feed is mixed C_4 to C_7 olefins in cracked naphtha cuts. A 95,000 BPSD unit was commissioned in January 1986 by BP Vohburg, West Germany.

From the above processes, it is evident that producers can process their C_4 fractions to octane boosters, chemical product intermediates, or both. A rundown of end products to the chemical product intermediates from C_4's are summarized in Table 3.4:

TABLE 3.4 POSSIBLE END PRODUCTS FROM CHEMICAL PRODUCT INTERMEDIATES OF C_4 FRACTIONS

Chemical Product Intermediates	**End Product**
1, 3 butadiene	- styrene-butadiene-rubber (SBR)
	- rubber other than SBR, e.g. nitrile rubber and polybutadiene rubber
	- styrene-butadiene-copolymer plastics (latex)
	- acrylonitrile-butadiene-styrene (ABS)
	- adiponitrile ---- hexamethylenediamine ---- nylon
MTBE	- gasoline pool
	- isobutylene
n-butane	- isomerization to isobutane
	- direct oxidation to methyl-methacrylate (MMA)
isobutene	- hydrogenation --- GTBA
	- etherification --- MTBE
	- alkylation --- i C_4 alkylate
	- oligomerization --- di/tri-isobutylene
	- polymerization --- diesel, jet fuel and polygasoline
	- oxidation --- methylmethacrylate (MMA)
	- polymerization --- polyisobutylene
isobutane	- propellant for aerosols
	- alkylate for increasing octane number
	- tertiary-butyl-alcohol (TBA)
butene-1	- comonomer for LLDPE
	- polybutene
octene	- plasticizer
	- non-ionogenic tensides (biodegradable)

4. DISCUSSION

On a worldwide basis, C_4's are used to produce MTBE -- an octane booster to gasoline. The production of other chemical products intermediates seems to be a way of completely using up the C_4's. The demand for MTBE is forecast to increase with the following:

- more automobile models that run on unleaded gasoline;
- legislations on environmental pollution;
- gasoline demand;
- structural modifications to refining.

In anticipation of this increase, MTBE plants are cropping up worldwide. Within the last few years many plants have been reported to be planned or to have started up. We envision most of the future plants to be integrated units. Table 3.5 shows a list of the world MTBE plants - operating and planned.

TABLE 3.5: MTBE PLANTS WORLDWIDE (adapted from 10) Page 1

Company	Location	Capacity (metric ton/yr)	Licensor	Contractor	Start Up Date
ANIC	Ravenna, Italy	100,000	Snamprogetti	Snamprogetti	1973
Huels	Marl, West Germany	120,000	Huels	--	1978
Arco Chemical	Channelview, TX, USA	200,000	Arco	--	1979
Phillips	Borger, TX, USA	20,000	Phillips	--	1979
Deutsche Texaco	Heide, W. Germany	12,000	Edelnau GmbH	--	1980
Neste Oy	Porvoo, Finland	80,000	Snamprogetti	--	1980
Good Hope Refineries	Good Hope, LA, USA	90,000	Huels	--	1980
Petrotex	Houston, TX, USA	280,000	Snamprogetti	--	1980
Fabrika SKO	Zrenjanin, Yugoslavia	38,000	Snamprogetti	--	1980
Phillips	Sweeney, TX, USA	100,000	Phillips	Procon Intern	1981
Dutch State Mines (DSM)	Geleen, Netherlands	75,000	Snamprogetti	--	1981
Schenectady Chemical	Freeport, TX, USA	50,000	Schenectady	--	1981
Charter-International	Houston, TX, USA	50,000	CR&L/Neochem	--	1981
Technoexport	Kralupy, Czechoslovakia	90,000	Huels	KDH Engineering	1981
VEAHB Industrieanlagen Import	Leuna, E. Germany	45,000	Huels	KDH Engineering	1982
Shell Netherland Chemie	Pernis, Netherlands	75,000	Shell International	--	1982
Texaco	Port Neches, TX, USA	250,000	Deutsche Texaco	--	1982
Exxon Chemical	Baytown, TX, USA	105,000	Huels	Davy McKee	1982
Champlin Petroleum	Corpus Christi, TX, USA	68,000	Huels	Davy McKee	1982
Chemokomplex	Leninvaros, Hungary	30,000	Snamprogetti	Snamprogetti	1983
OMV	Schivechat, Austria	50,000	Snamprogetti	Lurgi	1983
Mitsui Petrochemical	Chiba, Japan	5,000	Huels	--	1983
SIBP	Antwerp, Belgium	100,000	Phillips	Crawford & Russel	1983
FSK	Zrenjanin, Yugoslavia	35,000	Snamprogetti	Snamprogetti	1984
Texas Petrochemical	Houston, TX, USA	25,000	ARCO	--	1984
CO Petroquim/ Nordeste Petroflex	Brazil	50,000	Petroflex	--	1984
Naftochim Complex	Burgas, Bulgaria	80,000	Huels	Neftochim Project	1985
Arco Chemical	Corpus Christi, TX, USA	300,000	ARCO	--	1985

TABLE 3.5: MTBE PLANTS WORLDWIDE (adapted from 10) Page 2

Company	Location	Capacity (metric ton/yr) (*BBL/day)	Licensor	Contractor	Start Up Date
Diamond Shamrock	Sunray, TX, USA	45,000	ARCO	--	1986
Petronor	Sommorrosto, Spain	45,000	Huels	UOP	1986
ED Erdolchemie	Cologne, W. Germany	30,000	Erdolchemie	--	1986
Petrofina/Total	Grimsby, UK	150,000	--	Snamprogetti	1986
Enichem	Ravenna, Italy	125,000	Snamprogetti	Snamprogetti	1986
Pequiven	Jose, Venezuela	500,000	--	--	Planned
Texas Petrochemial	Houston, TX, USA	14,000	Air Products/ Houdry	--	1986
Petrofina	Big Spring, TX, USA	1,500*	--	--	1986
Sun Refinery	Marcus Hook, PA, USA	120,000	ARCO	--	1987
Elf Aquitaine	Feyzin, France	50,000	CR&L/IFP	--	1987
Amoco	Yorktown, PA, USA	34,000	CR&L/Neochem	Kellog	1987
Citco	Lake Charles, LA, USA	1,000*	ARCO	--	1987
Mobil	Beaumont, TX, USA	1,500*	--	--	1987
Amoco	Whiting, IN, USA	170,000	CR&L/Neochem	--	1987
Marathon	Detroit, MI, USA	2,000*	--	--	1987
Sabic/Neste/ENI/ APICORP	Al Jubail, Saudi Arabia	500,000	Snamprogetti	--	1988
Shell/Petronas	Kuantan, Malaysia	300,000	--	--	1990
Idemitsu/Neste/PNB	Malaysia	300,000	--	--	1990
Hellenic	Aspropyrgos Ref, Greece	65,000	Snamprogetti	Snamprogetti	Planned
Pet. Corp. of Singapore	Singapore	50,000	--	--	Planned
Caribbean Dev. & Comm.	Lago, Aruba	400,000	--	Eng. & Constr.	Planned
Statoil/Beva	Norway/West Germany	--	--	--	Planned
Lindsay Oil Refinery	Grimbsy, UK	100,000	BP/Ec Erdolchemie	--	Planned
Neste/Celanese Canada					
Hoeschst/ Trans Mtn. Pl	Edmonton, AB, Canada	500,000	--	--	Planned
Carbohyde Ireland Ltd.	Cork, Ireland	500,000	--	--	Planned

TABLE 3.5: MTBE PLANTS WORLDWIDE (adapted from 10) **Page 3**

Company	Location	Capacity (metric ton/yr)	Licensor	Contractor	Start Up Date
Petroguimica General	Ensenada, Argentina	40,000	Snamprogetti	Snamprogetti	Planned
Motoroil Hellas	Corinth, Greece	34,000	Snamprogetti	Technipetrol	Planned
Co National Petrog.	Sines, Portugal	40,000	--	--	Planned
RASCO	Ras Lanuf, Libya	60,000	--	Technimont	Planned
Empusa Columbia Pet.	Barranchabermesa, Col.	120,000	--	--	Planned
--	USSR	1,000,000	--	--	Planned
EMP	Tanagona, Spain	51,000	Huels/UOP	--	Planned

3.2 C_5 TECHNOLOGIES

Like C_4's, C_5's are produced from steam crackers of ethylene plants and also from FCC Units. The upgrading of C_5's to oxygenates has been a project of various studies.

Now, there are processes and even commercial plants to upgrade C_5's to Tertiary-Amyl-Methyl-Ether (TAME). In general, the process is similar to that for upgrading C_4's to MTBE. The feed, of course, is isoamylene and MeOH.

We shall review the upgrading of C_5's under two categories:

- commercially unproven processes, and
- commercially proven processes.

3.2.1 COMMERCIALLY UNPROVEN C_5 ETHERIFICATION PROCESSES

1.0 GULF CANADA'S ETHERIFICATION PROCESS

Gulf Canada seems to have been the first to develop and promote process technology for producing TAME (65), (64). The optimum etherification process includes MTBE, TAME and/or C_4 and C_5 methoxylation in the same reactor. These were pilot planted and patented (86).

Feed: Feed is C_5 olefins from FCC unit or thermal cracker by-products in ethylene production.

Process: The schematic diagram is shown in Figure 3.9. the olefin feed C_5^+ is first fractionated in order to separate the C_6^+ hydrocarbons from the C_5's. The C_6^+ material goes to gasoline blending. The C_5's are mixed with MeOH and enter the synthesis reactor. The reaction takes place in the liquid phase in the presence of a cation exchange resin catalyst (hydrogen form). Only 2-Methyl-2-Butene (2M2B) and 2-Methyl-1-Butene (2M1B) are reactive. 3-Methyl-1-Butene (3M1B) does not react nor do other C_5's present. The reaction is exothermic and an increase in temperature increases the reaction rate but at higher temepratures the reverse reaction is favoured (decomposition of formed TAME to Isoamylene and MeOH). The reactor operates in an upflow mode.

The reactor effluent is split - part goes back to the distillate column and part is either withdrawn and fed directly to the gasoline pool or goes to an optional methanol recovery unit.

The methanol recovery unit is made up of a counter-current extraction column and MeOH stripper.

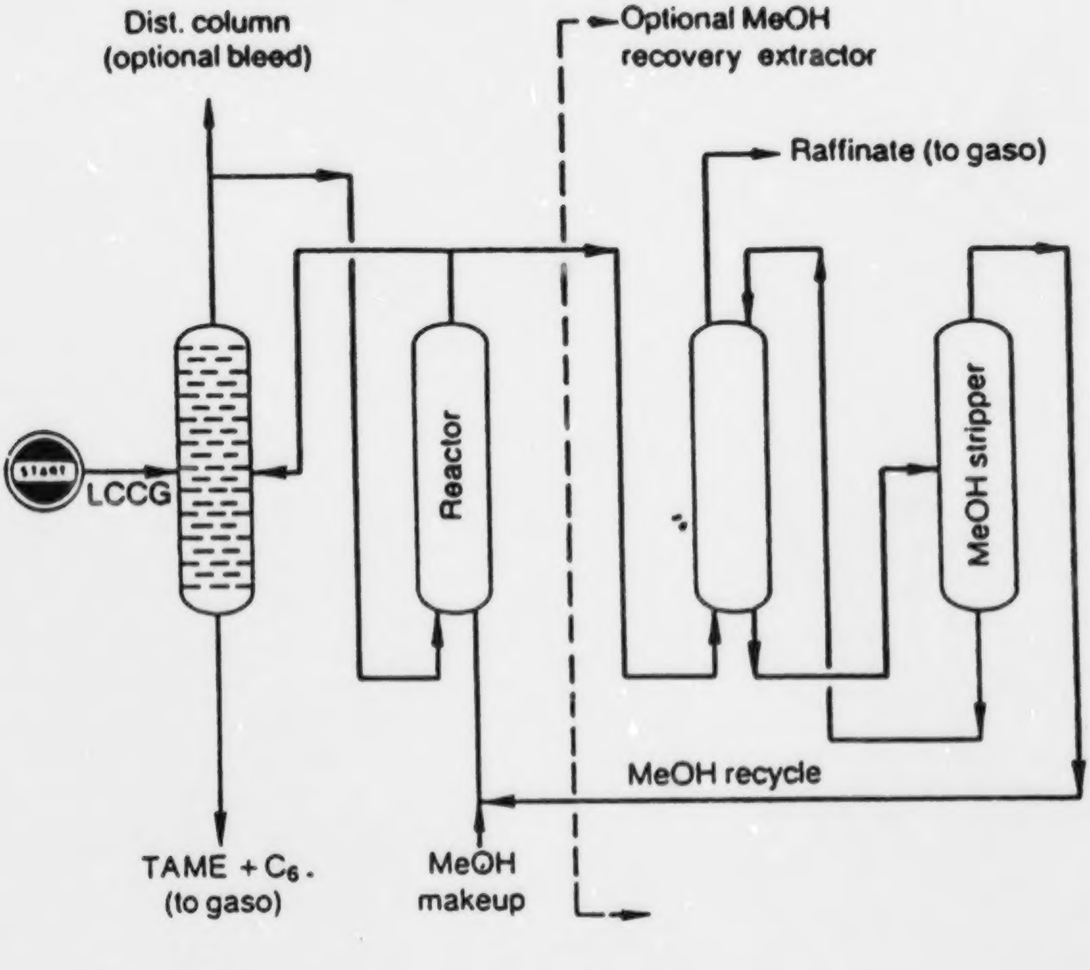

Dist. column
(optional bleed)
Optional MeOH
recovery extractor
Raffinate (to gaso)
START
LCCG
Reactor
MeOH stripper
MeOH recycle
TAME + C_6-
(to gaso)
MeOH
makeup

FIG.: 3.9
Gulf Canada's TAME process. (Source: 64)

The reactor effluent steam enters the bottom of the extractor and the methanol-lean steam from the stripper is used as the extraction medium. The raffinate from the extractor containing 7-15 wt% TAME and less than 0.1 wt% MeOH goes to the gasoline blending. The methanol rich extract is sent to a MeOH stripper. The Methanol from the top of the stripper is recycled to the reactor.

The TAME process conversion depends on the amount of C_5's recycled and lies within 40 - 70%.

Commercial Unit: Although pilot plant tests were run no commercial unit has been built to date using this process.

2. MOBIL OIL CORPORATION PROCESS (87), (88)

Feed: Feed is said to be olefinic streams containing isobutylene and/or isopentenes (2 Methyl-1 Butene or 2 Methyl 2-Butene).

Process: Methanol is mixed with isobutylene or isopentene, preheated and reacted at a temperature between 170 - 220°F in the presence of an acidic zeolite catalyst. Optimum temperature for the zeolite at atmospheric pressure is about 180°F. The conversion of isobutylene or 2M1B/2M2B is increased significantly when the reaction is carried out in the liquid phase (150 - 300 psig). The reacted components are removed and sent for further processing, e.g. alkylation. The stripper bottom fraction is made up mainly of MeOH and MTBE (TAME). This bottom steam goes to a dual column (adsorption-desorption unit) filled with 3A, 4A or 5A zeolite. The methanol is adsorbed in the adsorber with the effluent being MTBE (TAME) and less than 5% of other components, e.g. TBA. This adsorber effluent can be blended directly to a gasoline pool. With a combination of heat and reduced pressure the adsorbed methanol is desorbed. The desorbed MeOH is recycled to the reactor.

Catalyst: The acidic zeolite catalyst is:
ZSM-5 (US Patent No. 3,702,866) or
ZMS-11 (US Patent No. 3,709,979).

Selectivity: The selectivity of MTBE (TAME) increases with decreasing temperature. This is a result of the fact that olefin oligomerization reaction is reduced at lower temperature. The advantage of the HZSM-5 or HZSM-11 is the suppression of the oligomerization side reaction.

Product: The product is MTBE/TAME. The side product is TBA.

3. INSTITUTE FRANCAISE DU PETROLE PROCESS (11), (89)

Feed: Unsaturated C_5 fraction.

Process: The overall process is made up of two catalytic reaction stages and a distillation stage.

Stage 1: The C_5 is first selectively hydrogenated in order to convert the mono and diolefins into saturated hydrocarbons whereas M2B1 and M2B2 remain unconverted.

The catalyst for this hydrogenation is Pd on Alumina/Silica or Nickel on Alumina.

Stage 2: The second reaction stage involves etherification with an aliphatic C_1 - C_4 alcohol, e.g. CH_3OH at a temperature of 50 - 120°C and a sufficient pressure to maintain the reactants at least partly in the liquid phase.

The reactor is dual. First the reactants are passed through an expanded bed reactor and thereafter through a fixed bed reator. A portion of the effluent from the expanded bed reactor is recycled to its inlet. This dual reactor configuration allows for a better selectivity and an increased lifetime of the catalyst.

The catalyst in both reactors is a solid ion exchange resin (AMBERLYST 15) - a macroporous sulfonic resin present as particles of 0.4 to 1 mm.

Product: The product is made of 40 - 70% saturated hydrocarbons, 5 - 30% of mono-olefinic hydrocarbons, 15 - 35% of ethers and 2 - 10% of alcohol by weight. The alcohol is MeOH while the ether is TAME.

4. CHEMICAL RESEARCH AND LICENSING COMPANY TRANSETHERIFICATION PROCESS (19, 58, 93)

Feed: C_4's and C_5's from FCC Units or ethylene plants and MeOH or an alcohol of a higher boiling point than MeOH.

Process: An organic ether, e.g. MTBE, TAME is fed into a catalytic distillation unit. The process of concurrent reaction and distillation of the reaction components using the reaction catalyst as the distillation structure is known as catalytic distillation (58). The ether is partially dissociated into its olefin and alcohol components.

Concurrently, C_5's are fed into the catalyst bed. An ether of the C_5's (the heavier component) is formed and removed continuously from the bottom of the distillation column reactor, thereby forcing the reaction to completion. Unreacted materials (isobutene, C_5's and MeOH) are withdrawn as overhead and fed into a fractionator which is at a lower pressure (250 psi). In the fractionator substantially all of the MeOH and some of the isobutene and C_5's are taken overhead and recycled. The fractionator bottom is made up of a mixed isobutene - C_5 stream which could further be separated into a pure isobutene stream and a C_5 stream mainly free of isoamylene. Process advantages of the catalytic distillation system are various:

- ether removal as soon as it is formed minimizes decomposition of the ether and chaining to form polymer;

- reaction temperature is easily controlled by the boiling point of the hydrocarbon mixture at the system pressure;

- the rate of reaction is therefore controllable through regulating the system pressure;

- adjustment of throughput (residence time or $(\text{LHSV})^{-1}$) gives further control of product distribution;

- the reaction which is equilibrium limited is forced to run to completion (100% conversion) because of constant disruption of the equilibrium through product withdrawal;

Catalyst: Rohm and Haas Amberlyst 15 - acidic cation exchange resin in granular size of 0.25 to 1 mm. The finer catalysts provide high surface area but result in high presure drop across the bed. The catalysts are therefore placed into a plurality of pockets in a cloth belt, which is supported in the distillation column reactor by open mesh knitted stainless steel wire. This method allows for adequate flow and prevents loss of catalyst.

Results: The C_5's are normally available as a mixture containing several close-boiling compounds in a refinery stream. Extensive pilot plants tests have been carried out by CR&L using their catalytic distillation unit. The same configuration for removing excess MeOH and C_4 processing was used for C_5's. The results from the runs can be summarized as follows:

- Other compounds in the product include Methoxypentenes (MOP) which is formed by the reaction of piperylenes;

- Some Diethers are also formed;

- Isoamylene (IA) conversion to TAME is about 75% whereas isobutene (IB) conversion to MTBE is 95%;

- The Table on page 121 shows the product distribution from two refinery C_5 stream (taken from (19)).

C_5 ETHERIFICATION

C_5 Feed Stream	Conditions		Wt% in Product				
	Press	Temperature (${}^{o}F$)	MeOH	TAME	3 MOP-1	4 MOP-1	C_5's
A	75 psig	185-190	0.9	43.1	0.3	--	55.7
B	75 psig	200-120	0.9	2.2	54.8	7.4	34.7

Octane Data

Feed	Feed Octane		Product Octane	
	Motor	Research	Motor	Research
A	78.4	93.2	84.0	93.6
B	75.5	93.8	73.8	93.8

From the Table above if we quantify improvement (I) as:

$$I = \left[\frac{MON + RON}{2}\right]_{product} - \left[\frac{MON + RON}{2}\right]_{feed}$$

then for Feed A, I = 3,
and, for Feed B, I = -0.85.

Depending on the nature of the feed, there could be some improvement in the octane number.

3.2.2 Commercially Proven Processes for C_5's Etherification

BP Ventures, London, England licenses three processes under the umbrella of "ETHEROL PROCESS" (60, 77, 90, 91). The Etherol processes consist of:

a) Etherol Process for MTBE. Feedstock is C_4's or isobutylene.

b) Etherol Process for TAME and TAME gasoline. Feedstock is C_5's or isoamylene.

c) Etherol Process for mixed ethers. Feedstock is C_4 to C_7 fraction of FCC Units and steam crackers.

Of interest in this section is item (b).

3.2.2.1 BP's Etherol Process for TAME and TAME Gasoline

This process was developed by EC-Erdolchemie GmbH, Cologne, West Germany.

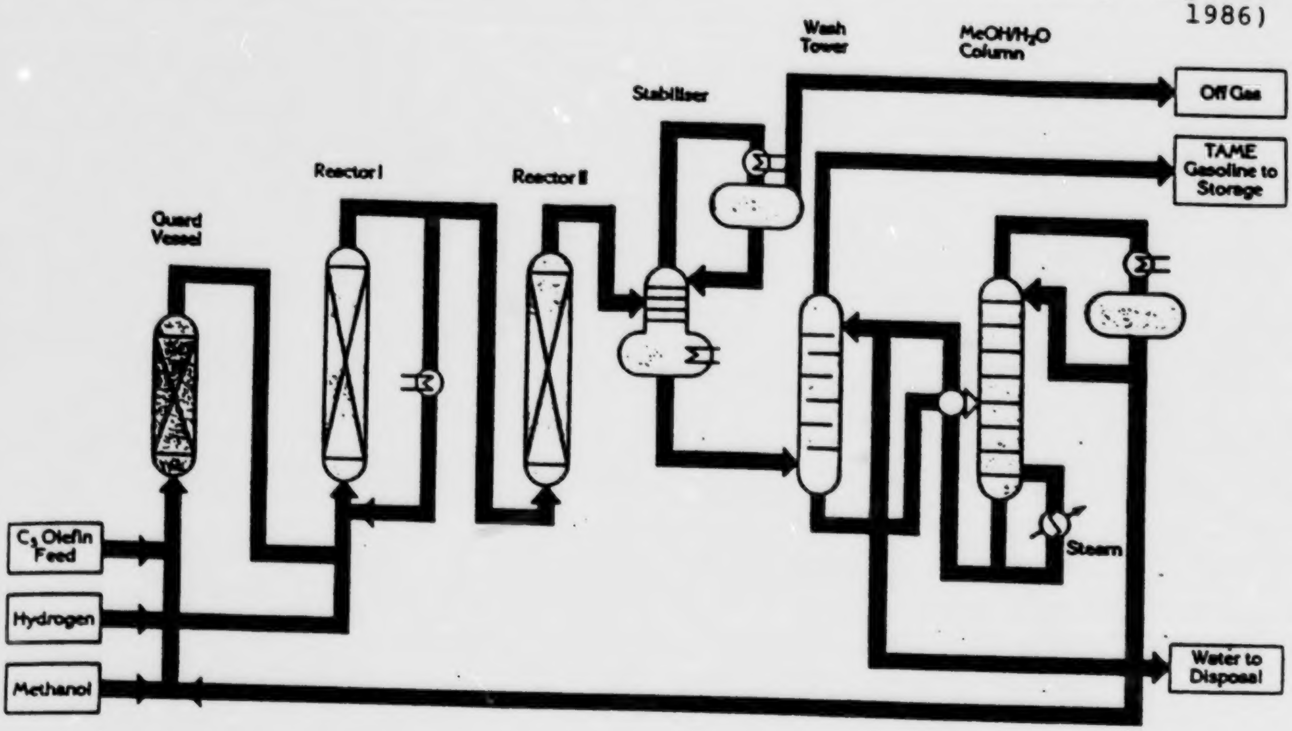
Feed: C_5's or isoamylene.

Process: As the process flow diagram shows, the scheme is made up of a reaction section, a distillation section and a methanol recovery section (Figure 3.10).

Reaction Section: C_5 olefin feed and Methanol are passed through a guard vessel where contaminants are removed. The reactants then flow through a two stage reactor system. Hydrogen is introduced in the first stage to hydrogenate unwanted diolefinic compounds. The two stage reactor system contains two types of catalysts - a novel trifunctional

FIG.: 3.10

ETHEROL PROCESS FOR TAME GASOLINE (Source: BP's Marketing Pamphlet 1986)


Wash Tower
MeOH/H₂O Column
Stabiliser
Off Gas
TAME Gasoline to Storage
Reactor I
Reactor II
Guard Vessel
Steam
C₅ Olefin Feed
Hydrogen
Methanol
Water to Disposal

[redacted]

catalyst and a conventional acidic ion-exchange resin. Through the upwards reactant flow pattern in the reactor, the heat of reaction is evenly dissipated thereby minimizing localized overheating. A slight excess of Methanol is used for the reaction.

Distillation Section: The effluent from the reaction section is stabilized and water washed in order to remove residual methanol. Water-Methanol mixture is taken out from the bottom of the wash tower while TAME is recovered as overhead.

Methanol Recovery Section: The Water-Methanol mixture passes to a recovery section where the mixture is separated into water and methanol. Methanol is recycled to the guard vessel while water is partly recycled to the wash tower.

A variant of this process produces TAME gasoline. In this instance, the reaction products containing TAME, unreacted C_5 hydrocarbons or aromatics forerunnings and some methanol are all directly used as high octane gasoline component termed TAME gasoline.

This process can therefore produce either pure TAME or TAME gasoline.

Catalyst: A new trifunctional catalyst used in the ETHEROL Process was jointly developed by EC Erdol Chemie and BAYER. The catalyst is a macroporous strongly acidic cation exchange resin with sulphonic groups and specifically impregnated with a nobel metal. This trifunctional catalyst is claimed to perform the following functions simultaneously:

- etherification of iso-olefins and methanol;
- selective hydrogenation of diolefins;
- hydroisomerization of olefins by a double bond shift.

The use of this catalyst enables diolefinic and acetylenic components in the C_5's feedstock to be selectively hydrogenated at temperatures below 100°C and pressures below 300 psi. The problem of yellowing of the product due to oligomerization is eliminated. The oligomeric products which build up on conventional acidic ion-exchange resin help to reduce the life of the catalyst. Catalyst life for this TAME process is projected to be five years.

Optimum performance is achieved through a careful selection of the process variables:

Highlights of Technological Features include the following:

- The TAME gasoline produced is claimed to be colourless with low existent gum* (5 mg/100ml).

- Catalyst life is expected to be five years.

- The value of a steam cracked C_5 cut is incrased by 8.5 octane barrels for every barrel of C_5 feed.

- For a C_5 cut from an FCC unit, this improvement is 6.1 octane barrels for every barrel of C_5 feed.

- A payback time of around two years is envisaged when a unit is installed to an existing refinery.

* Automotive gasoline may oxidize slowly in the presence of air to form undersirable oxidation product called gum. ASTM Specification for Automotive Gasoline (D-439) limits

gasoline to a maximum of 5 mg gum/100 ml of gasoline. The amount of existing gum in fuels is determined by ASTM Test for Existent Gum in Fuels by Jet Evaporation (D-381/IP-131). The tendency of gasoline to form gum during extended storage is measured by ASTM Test for Oxidation Stability of Gasoline (D-525).

Commercial Units:

a) A 45 BBL/DAY TAME unit (the first commercial plant to produce TAME) went onstream last year at EC Erdolchemmie's petrochemical plant, Dormagen, West Germany. (EC Erdolchemie is jointly owned by BAYER and BP).

b) A 5500 BBL/DAY TAME gasoline unit started up in March 1987 at Lindsey Oil Refinery, Grimsby, England. This plant is a joint operation of Belgium's PETROFINA and France's TOTAL.

3.3 COMBINED C_4's AND C_5's PROCESSING TECHNOLOGIES

Basically, refineries that have C_4's from their FCC Units also get C_5's. The same goes for ethylene plant's steam cracking unit. The problem of how best one can utilize both steams gave rise to technolgies for processing the combined stream. Most of the technologies in this field are at the developmental level and have not received wide acceptance in the form of commercial units. The reason is probably the existence of a wide spectrum of unreacted hydrocarbons, and the fact that some of the C_5 fractions could be blended into the gasoline pool with little processing (depending on the composition of the mixture).

A review of the predominant commercially proven as well as the non-commercially proven processes is given.

3.3.1 Commercially Unproven Processes for the Etherification of Mixed C_4's and C_5's

1. UNION CARBIDE CORPORATION PROCESS (92)

Process for Preparing Ethers

Feed: C_4's and C_5's from FCC Units and steam crackers of Ethylene Plants containing isobutylene and/or isoamylene.

Process: The methanol and C_4 and C_5 hydrocarbons are mixed in a reactor at a temperature of 65 - 90°C. The reaction pressure is such as to keep the reactants and products in the liquid phase. Excess methanol is used (higher than stochiometric) to increase conversion. The reaction product comprises methyl-tert-alkyl-ether, unreacted MeOH and C_4 - C_5 hydrocarbons and optionally dimethylether (DME). These reaction products are passed through a distillation unit where MTBE and/or TAME is removed from the bottom of the column. The unreacted MeOH, C_4's, C_5's and DME are recovered as overhead product from the distillation tower. This stream goes to an adsorption column where Methanol is selectively adsorbed on a molecular sieve adsorbent at a temperature of 75 - 120°C. The non-adsorbed C_4's and C_5's are removed as effluent stream and Methanol is subsequently desorbed.

The purge desorption effluent (MeOH) is recycled to the reactor.

Catalysts: The reaction step catalyst could be ion-exchange resins or inorganic heterogeneous catalysts such as boric acid or crystalline aluminosilicates of the zeolite molecular sieve type.

The adsorption step catalyst is the sodium cation form of Zeolite A having pore diameters of about 4 Angstroms (Zeolite 4A).

Product: The main product is MTBE and/or TAME. The stream from the adsorber if not recycled contains 500 - 1000 ppm or MeOH, 200 - 2000 ppm of DME and C_4/C_5 unreacted hydrocarbons.

The patent, although written with examples for the production of MTBE, encompasses the production of TAME and a mixture of MTBE and TAME.

Table 3.6 gives a summary of both patented and published processes for the etherification of mixed C_4's and C_5.

TABLE 3.6 PROCESSES FOR COMBINED C_4's AND C_5's PROCESSING
(Non-commercially proven)

Author/Assignee	**Date**	**Process Summary**	**Ref.**
Spender M.S. (ICI, UK)	01-02-84	Alcohol synthesis, separation, selective dehydrogenation, distillation and etherification.	(94)
Torck B. et al (IFP)	13-01-86	C_4 and C_5 Feed go into a main and a finishing reactor in series and then to a debutanizer. Bottom products = MTBE + C_5 + TAME.	(95)
Woods H.J. et al (Gulf Canada) Chase J.D. (Gulf Canada)	20-05-80	Isobutylene and isoamylene are etherified with MeOH. Unreacted MeOH is removed by contacting with liquid glycol and then separated by distillation.	(96) (97)
Nagji M.M. (Union Carbide Corp.) Rabo J.A. (Union Carbide Corp.)	19-06-86 25-09-86	Etherification of C_4's and C_5's with MeOH, isolation of reaction products followed by methanol separation using a selective adsorption/desorption system.	(92) (98)
Garwood W.E. (Mobile Oil Corp.)	01-04-81	The olefinic stream is restructured over a special zeolite catalyst to produce C_4 to C_7 olefins which are etherified with MeOH to produce ethers.	(99)

3.3.2 COMMERCIALLY PROVEN PROCESS FOR MIXED ETHERS

BP's ETHEROL PROCESS FOR MIXED ETHERS (60, 77, 90, 91)

Feed: Feed is claimed to be any light hydrocarbon stream rich in olefins. However, the predominant reaction is that of tertiary olefins in the C_4 - C_7 range with methanol.

Process: The mixed ether process has almost the same process configuration as the TAME and TAME gasoline process. The main sections are the same (see Figure 3.11). In the reaction section however, the reactors are operated to achieve optimum conversion because the conversion is different for the various C_4 - C_6 reactive olefins. Excess MeOH is desirable at this stage for maximum olefin conversion.

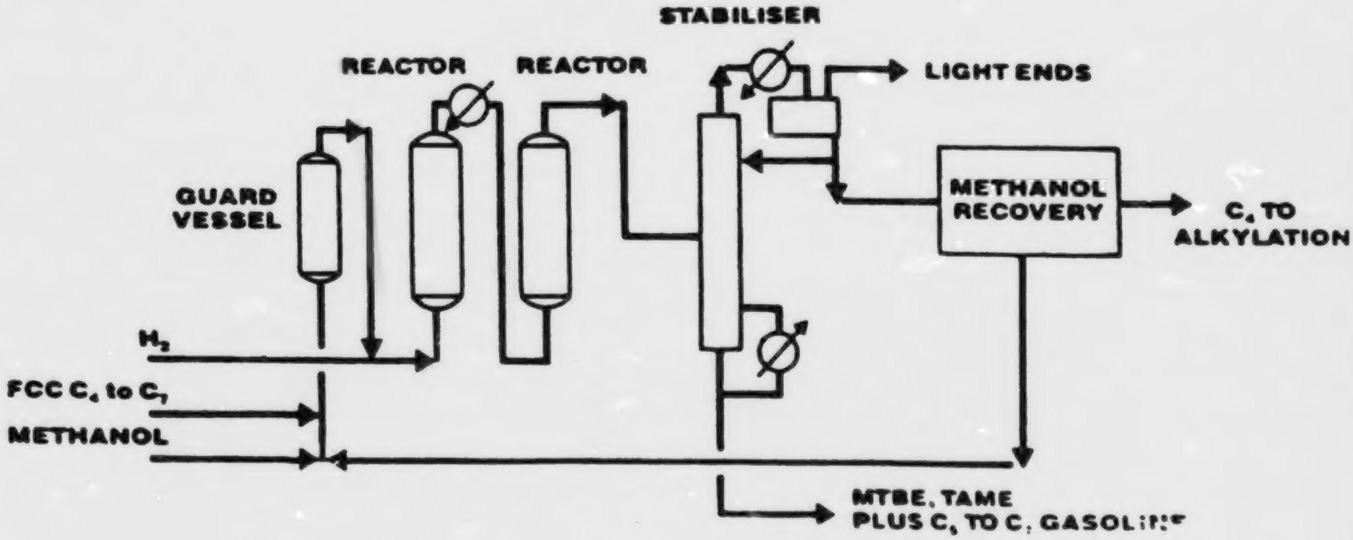
The reaction product goes to a distillation section (debutanizer). Here the C_4-raffinate methanol mixture goes overhead while the mixed methyl ether produce is withdrawn from the bottom of the tower.

Methanol recovery from the C_4-raffinate stream is achieved by selective adsorption on a special resin. The methanol is then desorbed by the C_4-rich feedstream and returned to the reactor section.

The quantity of the gasoline containing the mixed ethers depends mainly on the cutpoint of the feedstock.

Catalyst: The catalyst is the same as the TAME and TAME gasoline process. The capability of this catalyst to selectively hydrogenate unsaturated compounds, especially the diolefins, prevents gum formation which is common with conventional ion-exchange resins. The metal coating of the catalyst resin provides for better heat dissipation.

FIG.: 3.11 **BP ETHEROL PROCESS** (Source: 77)


STABILISER
REACTOR
REACTOR
LIGHT ENDS
GUARD VESSEL
METHANOL RECOVERY
C_4 TO ALKYLATION
H_2
FCC C_4 to C_7
METHANOL
MTBE, TAME
PLUS C_5 TO C_7 GASOLINE

Consequently, the adiabatic fixed bed reactors do not suffer any significant peak temperatures which lead to resin damage. Loss of palladium through rinsing out or abrasion is much lower with this catalyst than with conventional carriers. This results in prolonged life expectancy of the palladium coating as a result of improved fixation and lower abrasion.

Commercial Unit: The first commercial unit to produce a mixture of high-octane, tertiary-alkyl-methyl ethers started up at Deutsche BP's Vohburg refinery in West Germany - a 9,500 BBL/DAY Unit early 1986.

3.4 OVERALL EDONOMICS

The overall economics of oxygenates manufactured from C_4's, C_5's or both, could be broadly classified into two categories:

- production economics;
- process economics.

A. PRODUCTION ECONOMICS

The production economics of MTBE, TAME or both would depend to a large extent on the following:

(i) the nature of the feedstock;
(ii) the feedstock cost;
(iii) the cost of MTBE, TAME or both, relative to gasoline;
(iv) the value of by-products.

(i) The choice of the feedstock depends on what is available at a reasonable price; e.g. an FCC Unit's C_4's and C_5's used as feedstock to an MTBE-TAME processing unit would have a different isobutene/isoamylene concentration than a feedstock from an ethylene unit's steam cracker. (C_4's and C_5's from an ethane cracker would also be different from those of a naphtha stream cracker). Feed imported from outside battery limits would generally be more expensive than locally available feedstock. The following could be used as feedstock for MTBE:

- directly from C_4 cuts available from steam or catalytic crackers;
- by isomerization of normal butenes taken from the C_4 cut of steam or catalytic crackers after butadiene extraction;

- by dehydrogenation of isobutane taken from field butanes or produced by isomerication of normal butane.

It would only be natural to expect that the two latter routes would involve higher capital investment to build the process units necessary for the transformation of the butane to isobutane and thence to isobutylene.

(ii) The feedstock cost (C_4 and/or C_5 streams) swings over a wide price range within a year. This cost is governed by the law of supply and demand. It is also related to:

- NGL supply
- alkylation economics
- octane gasoline pool demand
- crude oil supply

A process based on field butanes would be attractive in certain circumstances, eg. if the field butanes are plentiful and priced at fuel value or in those parts of the world that have butenes and no place to sell them. In such a case the butenes can be converted to an octane component that is in demand in both Europe and the USA (100). Also, companies that have large MeOH plants and no markets would probably find it profitable to build a world scale MTBE/TAME plant which would use a large portion of the MeOH as feedstock.

(iii) Ludlow (100) summarized the assumptions under which MTBE production could be profitable as follows:

- spot price of unleaded regular gasoline selling at 1.3 times the crude oil price;
- mixed butanes at fuel value;
- MeOH in ample supply;
- MTBE selling at 1.4 times the unleaded spot regular gasoline price.

(iv) The price of by-products has an effect on the overall production economics of an MTBE/TAME plant. The goal is to process the feed to saleable products. Where a by-product stream cannot be sold as a result of plant location or no market value then the economics of such a plant should be carefully re-examined.

B. PROCESS ECONOMICS

It is not our intention here to evaluate the economics of each of the processes discussed in this chapter. The reader is advised to refer to the literature cited for these individual processes.

Process economics data comparison is outside the scope of this report. In order to choose a process the interested company should make a process economics study either by itself or through a neutral consultant. The wide range of licensors makes it sometimes difficult to come up with a best. Operating costs should be carefully looked into. Some processes have low capital investment costs but very high operating costs. The operating costs would generally include:

- feedstock;
- catalyst;
- chemical requirements;
- utilities consumption.

The technical reliability of the process is also important in order to avoid constant plant down-time. This implies that the anticipated onstream time must be adequate and the process must be flexible enough to accomodiate feedstock quality fluctuations which, in turn, would influence product quality.

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CHAPTER FOUR

PRODUCTS

4.1 ANALYSIS OF OXYGENATES

The monumental increase in research on processes and technologies for the manufacture of oxygenates for unleaded gasoline has led to efforts to find ways of analyzing the oxygenates quickly, qualitatively and quantatively.

The analytical methods include:

1) the determination of these oxygenated compounds in gasoline (where they are present in the range of 0 - 10%);

2) the determination of the oxygenated compounds in a product stream (where they could be present in a range of 40 - 99.9%).

4.1.1 Determination of Oxygenated Compounds in Gasoline

Infrared spectrometry has been used to determine alcohols, such as ethanol (1,2) and MTBE (3) in gasoline. Other procedures for the determination of oxygenates involve direct gas chromatography (with or without column switching) (6,7,8), dual capillary column gas chromatography (9), multi-dimensional capillary column gas chromatography (10) and liquid chromatography (11).

4.1.1.1 Infrared Spectrophotometric Method (12)

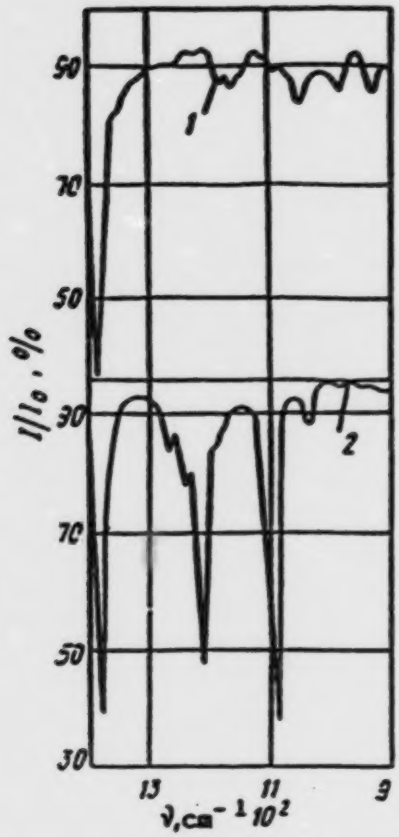
This method has been used for the routine control of MTBE content in automotive gasoline. It is based on a change in the selective absorption of infrared spectra by MTBE in the region of the stretching vibrations of the C-O-C bond.

Apparatus: Double-beam Infrared Spectrometer (medium or high dispersion) with a resolution not less than 1 cm^{-1} range and a reproducibility of transmission within ±1%.

Analytical Bond: 1090 cm^{-1} (corresponding to stretching vibrations of the C-O-C bond in ethers). MTBE contents in the range of 0.5 - 15% by weight can be determined.

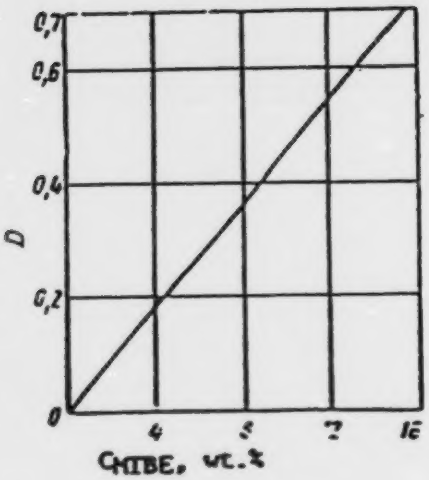
Optimal Settings: (using UR-20 Spectrophotometer)
- slit program for slit width = 4
- scanning rate - 160 cm^{-1}/min
- time constant = 2
- spectrum recording scale = 10mm/100 cm^{-1}

Results: The standard deviation of the results from determinations = 0.13 - 0.23 and the repeatability of parallel determination is 0.27 to 0.68% by weight. Figures 4.1 and 4.2 show the absorption spectra of leaded gasoline and MTBE in unleaded gasoline plus the calibration curve from (12).



* Figure 4.1 Infrared Absorption Spectra:

1) Leaded Gasoline
2) MTBE in Unleaded Gasoline



* Figure 4.2 Calibration line for the determination of MTBE content in gasoline.

Absorbing layer thickness = 0.022 cm

Absorption Band = 1090 cm^{-1}

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* Taken from (12)

4.1.1.2 Gas Chromatrographic Methods

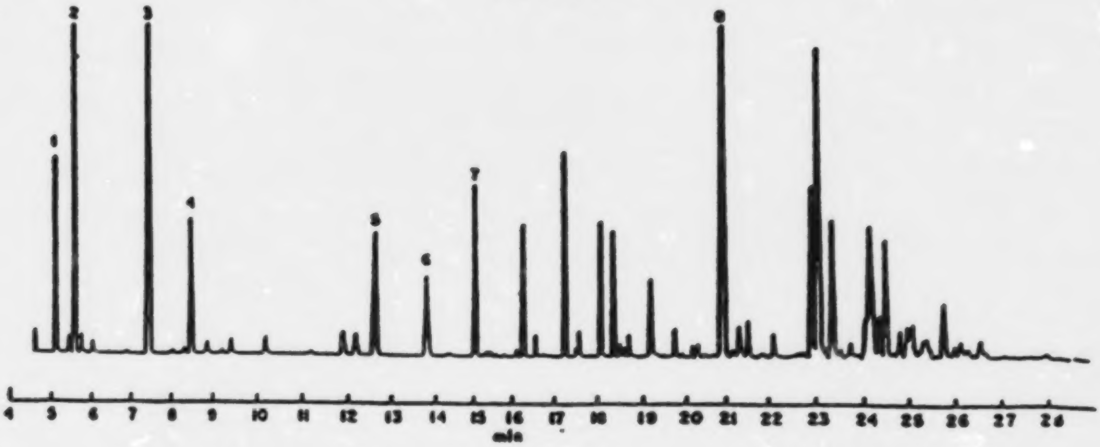
A Single Capillary Column Gas Chromatographic Method

Multiple column methods are commonly used for analyzing a mixture of polar and unpolar components. However, recently introduced fused silica capillary columns are so inert that they enable the separation of polar and non-polar compounds on non-polar substrates with little tailing. Hooks and Lockwood (13) of Shell Research, Thronton, England developed a method based on a single column GC. The method was successful in analyzing the components of gasoline (leaded, unleaded, light catalytically cracked) and oxygenated gasoline. The oxygenates analyzed include: MTBE, TAME, Methanol, Ethanol, propanol and butanol.

A detailed GC operating conditions for the analysis is given below while chromatograms of a premium gasoline and that of the same gasoline with oxygenates added are shown in Figures 4.3 and 4.4 (taken from (13)).

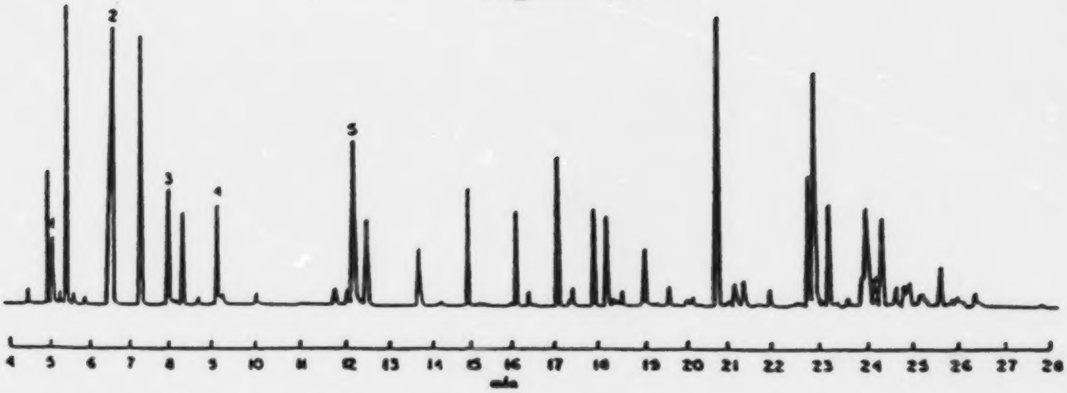
Gas Chromatograph: Hewlett-Packard Model 5880
Oven Temperature Program: 5 minutes at $8^{\circ}C$ and then
$8^{\circ}C$ - $16^{\circ}C$ at $1^{\circ}C$/min
$16^{\circ}C$ - $200^{\circ}C$ at $30^{\circ}C$/min
Maintain at $200^{\circ}C$ for 10 min
Analysis Time: 30 min with 40 min turnaround
Detector Type: Flame Ionization Detector (FID)
Sample Size: 0.2 microliter
Carrier Gas: Helium
Carrier Gas Flow: 1.4 ml/min at standard conditions
Injection Mode: 0.2 microliter injection volume with a split ratio of 120:1

*Figure 4.3



– Chromatogram of a premium gasoline on a 50 metre fused silica capillary column of 0.38 mm inside diameter with 0.52 μm dimethyl silicone gum as the stationary phase
Temperature: 5 min at 8°C, 1°C/min to 16°C, then 30°C/min to 200°C, and 10 min at the final temperature
Helium carrier gas at 1.4 ml/min, 130:1 split ratio
Labelled peaks are; 1 isobutane, 2 n–butane, 3 isopentane, 4 n–pentane, 5 2–methyl pentane, 6 3–methyl pentane, 7 n–hexane, 8 toluene

*Figure 4.4



– Chromatogram of the same gasoline as Fig. 1 with added oxygenates.
Labelled peaks are; 1 methanol (3%w), 2 ethanol (20%w) 3 2–propanol (5%w), 4 tertiary butanol (3%w), 5 MTBE (7%w). Column and conditions as Fig. 1

* Taken from (13)

Column Type: Single fused-silica capillary column coated with methylsilicone gum

Column Dimensions: 50m long and 0.3 mm nominal inside diameter with a nominal 0.52 micrometers thick film of dimethylsilicone gum as the stationary phase. The siloxane column was deactivated before coating.

Column Temperature: See oven temperature progam below.

B) Dual Capillary Column Gas Chromatographic Method

The method determines and identifies alcohols and MTBE in gasoline.

The technique involves the simultaneous injection of gasoline into two fused silica capillary columns of differing polarities (i.e., the two capillary columns and fitted in the same injection port and the sample is injected simultaneously onto both columns). The oxygenated compounds have different retention times on each column.

The gas chromatograph has an automatic sampler and dual terminal output. Operating conditions are given below together with Figure 4.5 showing the chromatogram of gasoline spiked with oxygenates (taken from (9)).

Gas Chromatograph: Hewlett-Packard Model 5880

Oven Temperature Program: $10^{\circ}C$ for 12 min
$10^{\circ}C - 50^{\circ}C$ at $5^{\circ}C/min$
$50^{\circ}C$ for 0.50 min
$50^{\circ}C - 230^{\circ}C$ at $25^{\circ}C/min$
$230^{\circ}C$ for 5 min

Pressure Program: 200 kPa for 25 min
200 kPa - 375 kPa at 50 kPa/min
375 kPa for 4.21 min
Injection Port Temperature: 240°C
Detector Type: Flame Ionization Detector (FID)
Dual (one for each column)
FID Temperature: 240°C
Sample Size: 0.2 microliter
Carrier Gas: Helium
Injection Mode: Split at 130:1
Column I (Polar): 60 m long x 0.25 mm ID, coated with a 1.0 micrometer film of Durawax-1 (J & W. Scientific). Durawax-1 is a mixed phase (90% dimethylpolysiloxane and 10% polyethylene glycol)
Column II (Non-Polar): 60 m long x 0.25 mm ID, coated with a 1.0 micrometer film of Durabond-5 (J & W Scientific) Durabond-5 is a 5% phenyl, 95% methyl silicone liquid phase.
Columnn Flow: 1.0 ml/min at 40°C
Analysis Time: 30 min; with 37 min turnaround

The method was found valid for the quantification of oxygenates in the 1 to 10 weight % concentration range. The reproducibility of rentention times was ±0.01 min (standard deviation). Of over 200 different oxygenated gasoline field samples run, the identification correlated well with infrared and mass spectral analyses. A method similar to this has been reported (10).

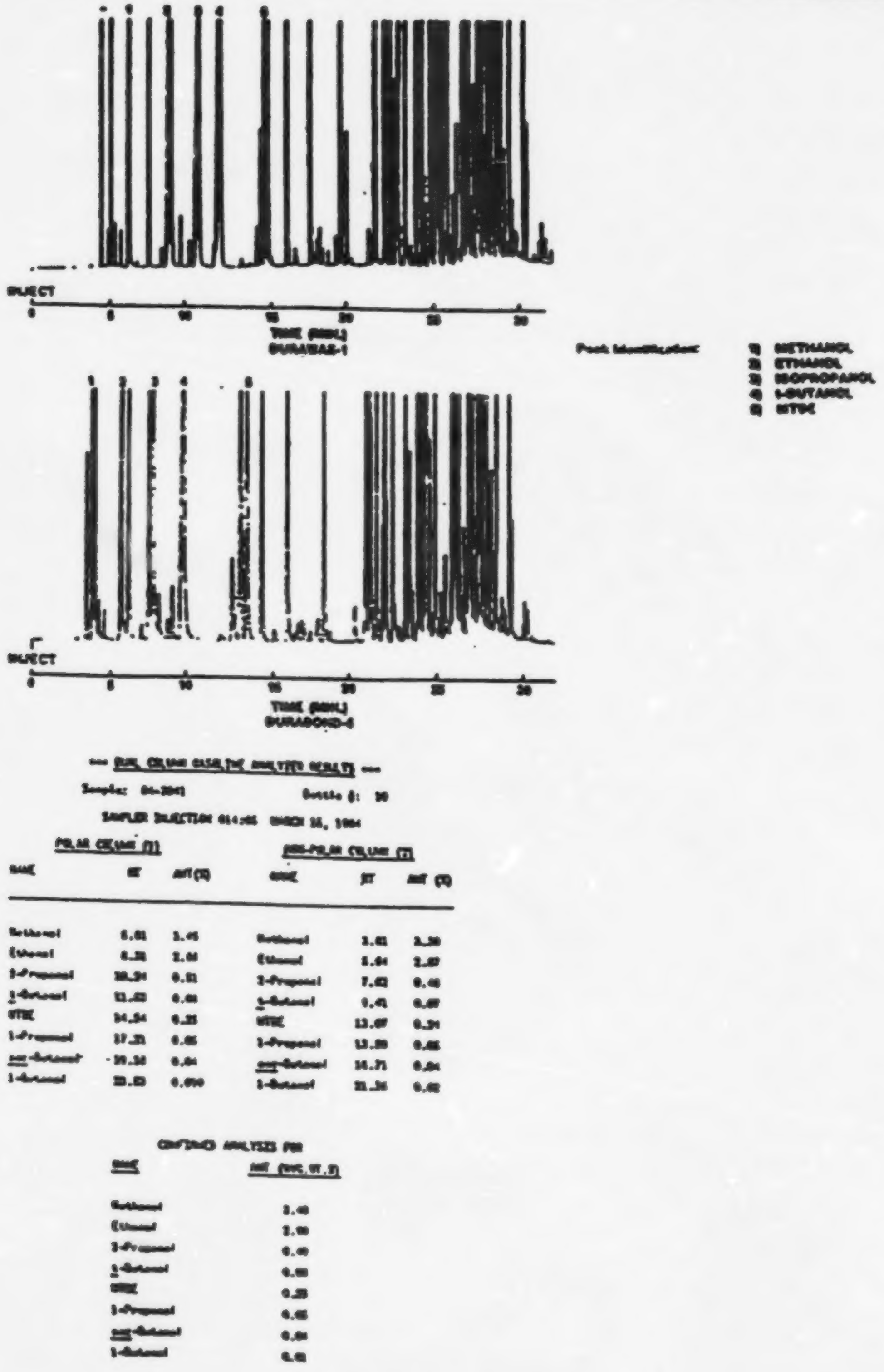


Figure 4.5 Dual column gas chromatograms of oxygen-free gasoline spiked with 6.0 - 9.0% oxygenates. (take from 9)

4.1.1.3 Liquid Chromatographic Method

The gas chromatographic methods of oxygenate analysis in gasoline have the inherent disadvantage of analysis time - 30 mins. Amoco Research Centre came up with another approach (14, 15) - a faster method by liquid chromatography.

In this procedure, two separate analyses for oxygenates are performed:

- one for alcohols, especially methanol, ethanol and t-butanol employing aqueous extraction/GC techniques, and
- a second analysis for MTBE using reversed-phase liquid chromatography (RPLC) with refractive index detection.

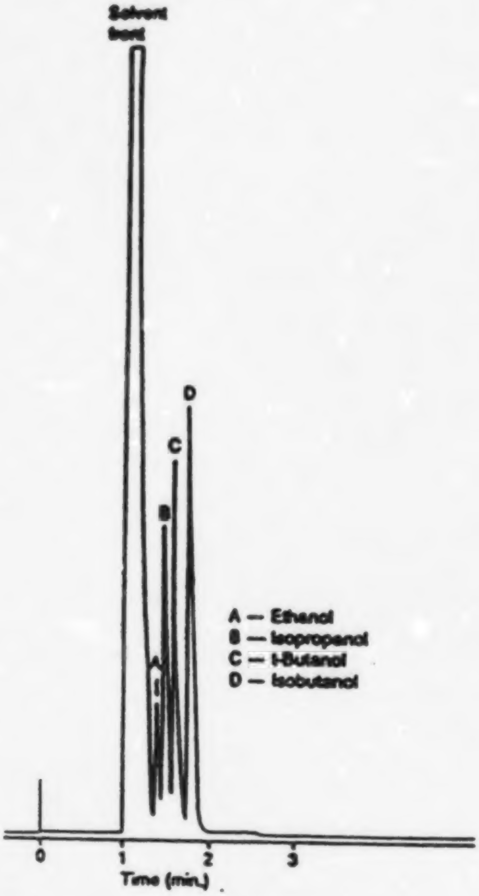
The RPLC apparatus consists of a pump, an injection valve, a backflush valve, a refractive index detector and a column (see (15)) for the full description).

Column Type: Hi-Chrom "reversible column" (Regis Chemical), 250 mm long x 4.6 mm ID, packed with Spherisorb ODS-II 5 micrometer particles;

Mobile Phase: 60% (v/v) acetonitrile (ACN) in water at a flowrate of 1.5 ml/min.

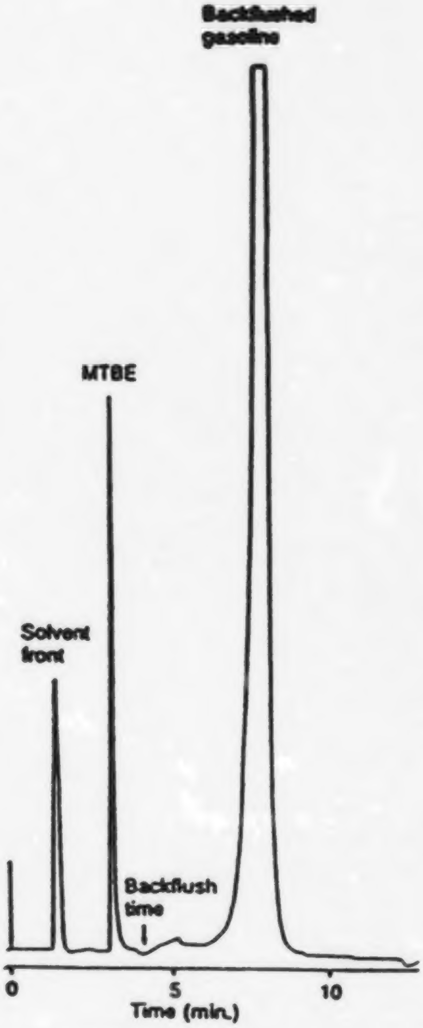
Through the use of column back flush instead of just flushing the columns with a strong solvent, the time required for equilibration to initial conditions was avoided. There was insignificant degradation in performance even after about 300 back flushes.

The RPLC method was used to determine MTBE in gasoline in a concentration range of 0.4 to 10 wt % - See Figure 6. Relative standard deviations for triplicate analyses were less than 1%. Benzene, toluene and ethanol in gasoline were also successfully analyzed within 15 minutes. (See Figure 4.6).



Chromatogram of alcohol blend. Mobile phase: 50% acetonitrile in water (v/v).

Figure 4.6(a)- taken from (11)



Chromatogram of gasoline containing MTBE. See text for conditions

Figure 4.6(b) - taken from (11)

4.1.2 The Determination of Oxygenated Compounds in Product Streams

Of methods that can be used for the analysis of oxygenated compounds in product streams, gas chromatographic methods predominate.

GC methods for the analysis of MTBE; MTBE, TAME and polymers; MIXED BUTYLENES; and MIXED C_5's were developed and documented by Chemical Research and Licensing Company, Maryland (16). These procedures taken directly from (16) are as follows:

4.1.2.1 MTBE

Column: 48 ft x 1/4-in stainless steel tubing packed with 10% Polyterge + 2% Polyterge J-300 coated on 100/120 mesh Supelcoport

Sample Size: 0.5 L

Carrier: Helium Rate: 30 ml/min.

Detector: Flame Ionization

Temps: Oven $40^{\circ}C$
Injection port $100^{\circ}C$
Detector $200^{\circ}C$

Elution Time, min.	Component
4.7 - 6.4	C_4's
7.8 - 9.7	C_5's MeOH
14.5	MTBE
16.7	MSBE (Methyl-Secondary-Butyl-Ether)

4.1.2.2 DME

Column: 48 ft x 1/4-in stainless steel tubing packed with 10% SP-2100 + Polyterge J-300 coated on 100/120 mesh Supelcoport

Sample Size: 0.5 L

Carrier: Helium Rate: 30 ml/min.

Detector: Flame Ionization

Temps:		
	Oven	25°C
	Injection port	100°C
	Detector	150°C

Elution Time, min.	Component
2.2	$C_1 + C_2$
3.3 - 3.9	C_3's
5.7	DME
6.1	i-C_4
6.9 - 12.8	Other C_4's

4.1.2.3 MTBE, TAME, Polymer Characterization

Column: 50 mm x 0.25 O.D. quartz tubing coated with SE-30

Sample Size: 0.67 L split 100 to 1

Carrier: Helium Rate: 30 ml/min.

Detector: Flame Ionization

Temps:		
	Oven	50°C
	Injection port	150°C
	Detector	200°C

Elution Time, min.	Component
7.4	MeOH
7.6 - 7.8	C_4's
8.0 - 8.6	C_5's
9.2	MTBE
9.7	MSBE
12.2	TAME
15	DIB-1
16	DIB-2
	Other dimers elute relative to B.P.

4.1.2.4 Mixed Butylenes

Column: 40 ft x 1/4-in stainless steel tubing packed with 20% Sebaconitrile coated on 80/100 mesh Chromosorb P aw + 6 ft x 1/8-in stainless steel tubing packed with 20% Phenyl Isocyanate coated on 80/100 mesh Poracil C

Sample Size: 0.67 L

Carrier: Helium Rate: 30 ml/min.

Detector: Flame Ionization

Temps:		
	Oven	Room Temperature
	Injection port	80°C
	Detector	150°C

Elution Time, min.	Component
7.9	Propane
9.9	Propylene
10.6	Isobutane
12.9	n-Butane
17.8	Butene-1
19.7	Isobutylene
21.4	t-Butene-2
24.0	c-Butene-2
28.5	1,3 butadine

4.1.2.5 Mixed C_5's

Column: 20 ft x 1/8-in stainless steel tubing packed with 20% Ucon LB-550X coated on 80/100 mesh Chromosorb P AW

Sample Size: 0.67 L

Carrier: Helium Rate: 30 ml/min.

Temps:		
	Oven	40°C
	Injection port	100°C
	Detector	150°C

Elution Time, min.	Component
6.0 - 9.8	C_1 - C_4
12	i-Pentane
15.1	n-Pentane
16.1	Pentane-1
17.3	2-MB-2
19.1	t-Pentene-2
20.3	c-Pentene-2
21.9	2-MB-2
28.5	isoprene
26.8	?
29.4	?
31.4	Cyclopentane
33.7	Cyclopentane
37.8	?

4.1.3 Analysis of Gasohol and Denaturated Fuel Ethanol

Gasohol defined here is a motor fuel containing 10% volume of denaturated ethanol in gasoline.

A recent "Information Document on Gasohol" issued by the American Society for Testing and Materials (ASTM) indicates that no standard ASTM procedure currently exists for the analysis of ethanol content of gasohol. ASTM Committee D-2 Research and Development Division IV on Hydrocarbon Analysis has been requested to develop procedures. However, the following procedures were given in the text as Appendices X4, X5, X6, X7, X8:

Appendix X4:	"Go/no go method to measure the water tolerance of gasohol."
Appendix X5:	"Alcohol content of gasohol by gas-liquid chromatography."
Appendix X6:	"Alcohol content of gasohol by gas-liquid chromatography (water-extraction method)."
Appendix X7:	"Collaborative study of the quantitative determination of ethanol by gas-solid chromatography."
Appendix X8:	"Field Test for the determination of the total ethanol, methanol and water content of gasohol."

In D-2/E-44 Proposal P170 from ASTM with the title "Proposed Specification for Denatured Fuel Ethanol to be Blended with Gasolines for Use as an Automotive Spark Ignition Engine Fuel", a test method was proposed for the "determination of ethanol content of denatured fuel ethanol by gas chromatography". This proposed method is still awaiting approval.

4.2 PERFORMANCE OF OXYGENATED GASOLINE

As early as 1968, AGIP in Italy had carried out research work on the effects of the addition of oxygenates to automotive fuels. Methanol and MTBE were tested before the first commercial MTBE plant went onstream in 1973. All subsequent studies indicate that amongst the oxygenates, alcohols behave differently from the others. Amongst the ethers, MTBE has been the most widely studied while amongst the alcohols it is methanol.

The influence of the addition of oxygenates to gasoline on automobile performance, fuel quality and the environment are discussed below.

4.2.1 Antiknock Quality

The definitions and test methods for antiknock performance for automotive gasoline are set forth in ASTM Specifications for Automotive Gasoline (D-439). Measurement of antiknock quality has been standardized using two single cylinder methods:

a) ASTM Test for Knock Characteristics of Motor Fuels by the Research Method (D-2699/IP-237).

b) ASTM Test for Knock Characteristics of Motor and Aviation-Type Fuels by the Motor Method (D-2700/IP-236).

Both of these tests employ a variable-compression-ratio engine. The motor method operates at a higher speed and inlet mixture temperature than the research method. the procedures relate the knocking characteristics of a test gasoline to standard fuels which are blends of two pure hydrocarbons - isooctane (2,2,4-trimethylpentane) and n-heptane. By definition, the octane number of isooctane is 100, and the octane number of n-heptane is zero. Results from engine test method (a) above give Research Octane Number (RON), while results from engine test method (b) give Motor Octane Number (MON). The actual road octane number of a gasoline will be between RON and MON, hence the Antiknock Index (AI). Antiknock Index is obtained by summing one half RON and MON of a gasoline, i.e.,

$$\text{Antiknock Index (AI)} = (\text{RON} + \text{MON})/2$$

The antiknock quality of gasoline is therefore measured in terms of octane number. If antiknock quality is too low, knock occurs. Knock is a high pitch, metallic rapping noise. In addition to being audibly annoying, in severe cases, knock may lead to uncontrolled preignition which can cause burning of piston crowns and other engine damage. Knock also increases the rate of engine wear. The potential durability, power, and fuel economy of a given engine is realized only when the gasoline antiknock quality is adequate (33).

Antiknock quality can be interpreted in simple terms as the resistance of the gasoline to too rapid combustion in the cylinder of an engine. Higher compression engines have higher performance and better thermal efficiencies but require fuels of higher octane rating in order to prevent spontaneous ignition of the fuel-air mixture (termed detonation).

Studies of the octane benefit of ether-containing fuels in vehicle operation confirm the octane contributions which have been observed in laboratory engine tests (17). Although discrete, single-valued octane blending values can be assigned to alkyl-tertiary-alkyl ethers for specific measurements, it sometimes seems more appropriate to assign a range of values. This is because the octane response of the fuel blend will vary with the characteristics of the base gasoline as well as with the quanity of ether blended into the system. Table 4.2.1 shows laboratory octane blending values of different alkyl-tertiary-alkyl ethers:

TABLE 4.2.1 LABORATORY OCTANE BLENDING VALUES OF SOME ALKYL-TERTIARY-ALKYL-ETHERS AND ALCOHOLS

BLENDING ETHER OR ALCOHOLS		OCTANE NUMBER*		REF
		RON	MON	
Methyl-Tert-Butyl-Ether	(MTBE)	115-135	98-110	19
Tertiary-Amyl-Methyl-Ether	(TAME)	105-122	96-105	17
Ethyl-Tert-Butyl-Ether	(ETBE)	118	105	18
Isopropyl-Tert-Butyl-Ether	(ITBE)	127	--	18
Methyl-Tert-Isooctyl-Ether	(MTIE)	111-117	97-104	18
Methanol	(MeOH)	133-138	96-120	20
Ethanol	(EtOH)	128-136	96-112	20

* Data sources varied and different based gasolines were used.

As the table above shows, the molecular configuration is more important than molecular weight in deciding whether an ether molecule will give a high octane blending value or not.

Methanol and Ethanol have higher octane blending values than MTBE and TAME (see Table 4.2.1), but present techical problems. The technical problems are similar but are less severe for Ethanol than for Methanol.

4.2.2 Volatility Effects

The measure of how readily a fuel vapourizes at different temperatures is termed volatility. The specification for fuel volatility is the Reid Vapour Pressure which gives fuel evaporation at 100°F (37.8°C). The volatility of the fuel is important because it affects the following:

- the driveability of the vehicle;
- evaporative emissions into the atmosphere.

McCallum P.W. et al (21) described drieveability as the responsiveness of a vehicle to throttle inputs from the driver. Most severe driveability problems arise when the engine is cold and when it is warming up. Alcohols place a limit at the temperature at which an engine can be started (MeOH = -10°C, EtOH = -15°C and gasoline = -30°C) (21, 22). Alcohol-gasoline blends are therefore more likely prone to cold start problem than ethers.

Higher temperatures (hot weather conditions) can contribute to a degree of fuel vaporization in components upstream of the intake manifold which would then interfere with the delivery and metering of fuel to the engine. This condition is known as "vapour-lock". Alcohol-gasoline blends have a higher tendency towards vapour-lock than gasoline or ether-gasoline blend (21, 23). The higher boiling ethers do not pose as great a vapour-locking tendency problem as does MTBE. Tests on a 15% blend of TAME in both a low RVP and in a typical summer grade gasoline showed that the use of a higher ether does not increase the vapour-lock problem (21).

Higher fuel volatility therefore improves driveability in winter but causes vapour-lock in summer. Blends should therefore be adjusted seasonally like unblended gasoline to reflect weather conditions.

4.2.3 Safety and Toxicological Effects

Methanol has a low odour intensity and its flames are not visible in bright sunlight. This is not safe for fire fighters or even anyone who might be exposed to high levels of methanol vapour without realizing it. Blending, however, alleviates this problem.

Exposure of the skin to liquid ethanol causes irritation due to its solvent effect which removes most of the skin's natural oil. In blends, however, the hydrocarbon components' concentration determine the health effects. MeOH is toxic, ie. 28-57 g ingested is lethal, while a lower concentration would cause blindness. The ethers, on the other hand, have perceptible odours even when they are present in gasoline at low concentrations.

Comprehensive laboratory tests performed concluded that MTBE and TAME or their blends present no greater toxicological hazards than does unleaded gasoline (24, 25).

4.2.4 Environmental Effects

Emissions from automobiles which are of concern to environmentalists include:

- unburned hydrocarbons (UBHC) or fuels (UBF)
- carbon monoxide (CO)
- oxides of nitrogen (NO_x)

The quantity of emissions depends both on the fuel itself and on the Air-Fuel (A/F) ratio. In spark ignition (SI) engine tests the A/F ratio is usually normalized as equivalence ratio.

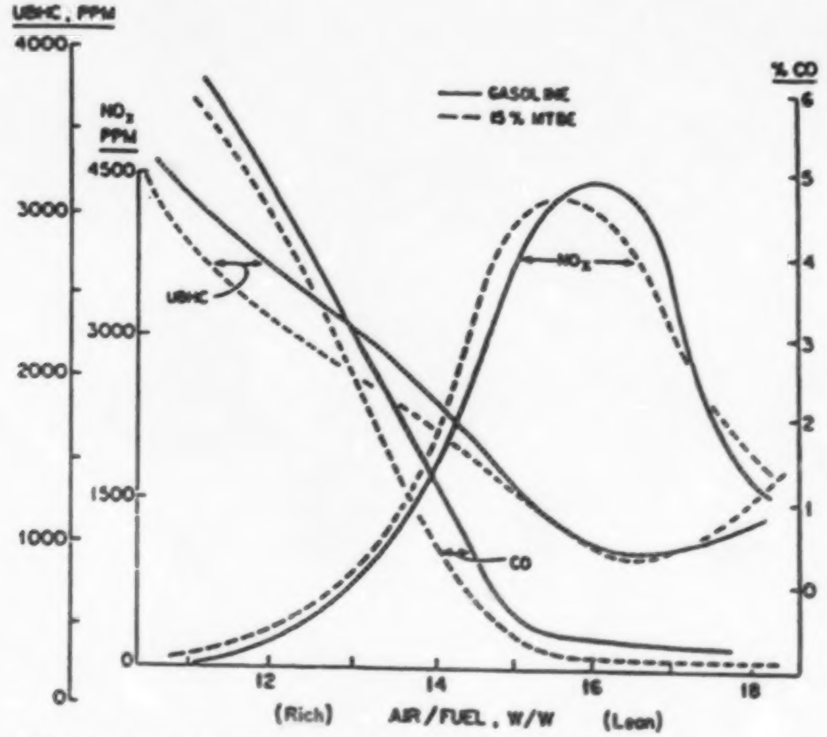


Figure 4.7 — *Emissions Effects With MTBE in CFR Engine Operation*

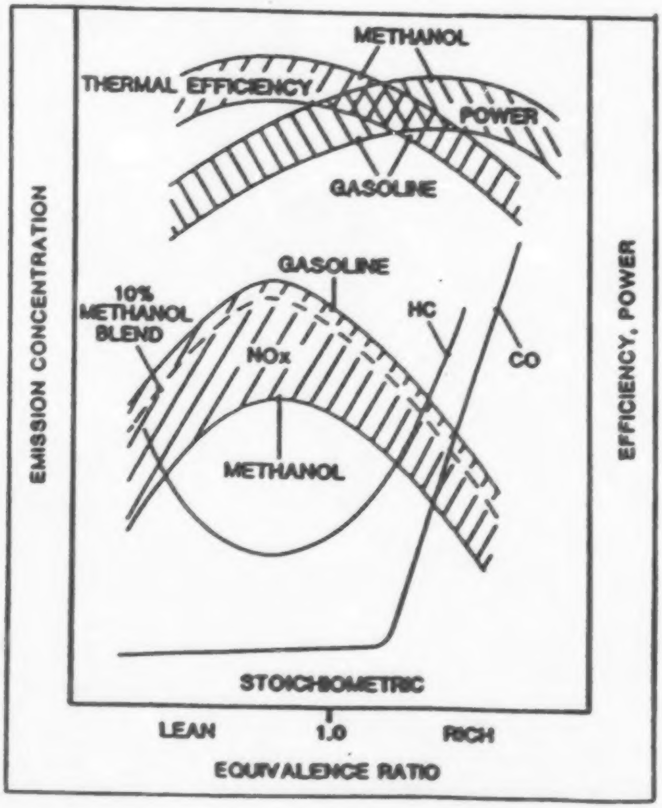


Figure 4.8
Effects of alcohol fuels on engine.

Equivalence ratio is the actual fuel/air ratio divided by the stoichiometric fuel/air ratio. Figures 4.7 and 4.8 show the emission effects of MeOH, gasoline, 10% MeOH in gasoline and 15% MTBE in gasoline on engine operation.

From the figures, it is obvious that on blending MeOH with gasoline, both CO and UBHC of the blend decrease with leaning to equivalence ratios somewhat below the stoichiometric 1.0. NO_x emissions, on the other hand, reach a maximum at equivalence ratios a little below 1.0. Tests on the effect of 10% EtOH in gasoline (Gasohol) on emissions showed overall decreases in UBHC and CO and increases in NO_x, all in the exhaust, and increases in fuel evaporative emissions (20, 26).

Data analysis has convinced EPA that for vehicles tested with 7% MTBE in gasoline, UBHC emissions were not increased while CO and NO_x emissions were decreased. EPA concluded that MTBE presents no threat to the long-term durability of vehicle emission control systems. No detrimental effects are reported for TAME (28).

Aldehyde emissions from a 15% MTBE-gasoline blend were higher compared to the base gasoline but not statistically significant (29). Smogs made from both exhaust and evaporative fuel emissions from a 15% MTBE fuel were tested in relation to eye irriation and were found to be no worse than the base gasoline. (24).

4.2.5 Effect on Distribution Systems

Methanol is highly corrosive to magnesium and to terne metal which is a lead-tin alloy used to coat steel fuel tanks and lines. Dry MeOH blends are not corrosive but the presence of enough water to cause phase separation makes them seriously corrosive to steel, aluminum or zinc. These are all common fuel system metals (21). Both MeOH and EtOH, although quite stable in storage as pure compounds, are said to increase the rate of gum formation in blends during storage (20). The blends also increase the solubility of gum in the fuel so that gum-bound deposits of rust and other sediments are loosened and eventually end up plugging vehicle fuel filters.

Viton, used in critical parts of some carburetors, swells excessively in methanol-rich fuel; cork and leather tend to shrink and/or harden, and polyester-bonded fiberglass softens, blisters and delaminates (20). Polyester-bonded fiberglass tanks used for underground storage at gasoline tanking stations are reported to be suitable for up to 10% MeOH blends, though the tank life may be reduced (30). Polyurethane, which is used in some gasoline fuel system components, is reported to detoriate faster in methanol/gasoline blends than in methanol-rich fuels. Polyurethane impregnated pump diaphragms which have been satisfactory with gasoline were reported to have failed with ethanol blends in Brazil (20).

However, autofinishes, plastics, elastomers and metals typical of systems for fuel management in a vehicle were exposed to gasoline and MTBE - gasoline blends (18,24,27,28) and no detrimental effects attributable to MTBE were observed. TAME's behaviour is similar to that of MTBE.

4.2.6 Stability

Ethers have the propensity to form dangerous peroxides on exposure to air. During long-term or "accelerated" storage conditions MTBE and TAME have shown resistance to peroxide formation (19,24,28).

Gum formation is also of concern with oxygenated additives in gasoline. Although ether-gaoline blends have shown increased washed gum values, the addition of conventional gasoline additives is said to impart high storage stability both to MTBE and TAME-gasoline blends (19, 24). Chase J.D. and Galvez B.B. (31) reported that blends of TAME and MTBE with gasoline could be stored in excess of two years.

4.2.7 Water Tolerance

Although Ethanol and Methanol are completely miscible with gasoline at normal temperatures, they separate easily in the presence of even small amounts of water. The gasoline-rich phase is at the top and the alcohol-rich phase is at the bottom. The alcohol-water layer tends to pick up dirt or sediment easily and can stall the engine upon reaching the carburetor. It is also corrosive to metals used for carburetor bodies and fuel system parts (20).

The water tolerance of blends, ie., the amount of water a blend can dissolve before it separates into two phases, is dependent on several factors as documented in (20):

i) temperature;
ii) type of alcohol (methanol or ethanol);
iii) concentration of the alcohol in the blend;
iv) gasoline characteristics (especially the aromatic content);
v) type of additives (cosolvent) and quantity.

The above dependencies can be summarized as follows:

- Water tolerance increases with increasing temperature;
- Ethanol blends have greater water tolerance than methanol blends.
- Water tolerance increases with alcohol concentration at temperatures above 5°C;
- There is an increase in water tolerance with the aromatic content of the gasoline;
- Addition of a cosolvent higher alcohol increases the water tolerance considerably.

An MTBE-gasoline blend is much more water-tolerant than an alcohol-gasoline blend. However, an MTBE-gasoline blend has a tendency to cloud and release water when cooled below its saturation temperature. Therefore, incidents of hazy gasoline may be more common with MTBE-gasoline fuel than with pure gasoline. Mutual solubilities of higher ethers and water are much less than those of MTBE. Gasoline blends of higher ethers TAME, ETBE, etc. would, therefore, be less water sensitive than MTBE-gasoline blend (18,19,32).

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CHAPTER FIVE

DISCUSSION AND CONCLUSION

5.0 DISCUSSION AND CONCLUSION

The upgrading of C_4's and C_5's to saleable products is definitely a challenge to the refining and petrochemical industry. Depending on the needs of the plant or company faced with this challenge a decision has to be made. There are basically three routes to go:

A) upgrading to oxygenates for octane enchancement;
B) upgrading to petrochemical feedstocks or intermediates;
C) integrated processing yielding both oxygenates and petrochemical intermediates/feedstocks.

Stand alone refineries would most probably choose the first route as it offers them a way of upgrading the octane of their gasoline pool In octane upgrading, the refiner has several options:

- use of a high octane FCC catalyst;

- use of methanol and isopropylalcohol (IPA) or tert-butyl-alcohol (TBA) blend. This requires outside purchase and availability and price might be a drawback;

- conversion of LPG to aromatics;

- improving reformer operation through:
    - o revamp
    - o change from semi-regenative to continuous reformer operations
    - o increase of reformer severity to produce a reformate higher in octane value;

- revamp FCC units (and reformers) in order to obtain octane increases above those attainable when only the catalyst is changed;

- C_5/C_6 isomerization with a good choice of recycle. A once through design does not contribute many octane barrels;

- selective hydrogenation of FCC olefin feed to the HF alkylation unit;

- addition of a propylene alkylation unit. This can give a significant increase in octane barrels to the gasoline pool but the feedstock in fuel gas must be available;

- addition of a catalytic polymerization unit to produce poly gasoline feeding propylene. However, poly gasoline has a low motor octane clear rating with an (R + M)/2 value of 87.8. It is said to produce a product with a good octane blending value and also does not require isobutane;

- catalytic dimerization of available FCC propylene. This provides the same process benefits as a catalytic polymerization unit. However, blending values and volumetric yields for dimates are higher than those for poly gasoline;

- dehydrogenation of field butanes to produce isobutylene which is then used for MTBE or TBA production;

Each of the options above has to be evaluated for:

- impact on pool octane;
- cost in cents per octane-barrel added;
- sensitivity to feedstock;
- overall costs (capital, operating, by-products).

Petrochemical plants which are more interested in producing petrochemical feedstocks or intermediates will find route (B) more attractive.

Large complexes, especially in Europe where petrochemical companies are integrated with refineries, would find the last route (C) most attractive. This route, we predict, is the route for future plants. The economic advantage of an integrated complex is enormous. The complex would contain isomerization, dehydrogenation, etherification and probably methanol plants. A common steam system can be used and this entails careful optimization such that the high pressure steam would be used in turbines, medium pressure in the process, and low pressure steam in the steam reboilers. This makes it attractive to use steam turbines for all major process drivers.

Integration makes it possible to optimize the numerous process recycle streams between the units. It also paves the way to the maximum utilization of off-gas streams (either as fuel or feedstock), so that product yield and energy efficiency are greatly enhanced. Such a complex, however, involves immediate high capital investment and is only plausible for large companies. A reasonable capital outlay involved in this type of plant is the very large tank farm - due to the intermediate storage tanks necessary to enable plant operations to continue when any part of the complex is down (starting, shut-down or maintenance).

Small refineries or ethylene plants may not find it economical to build an MTBE unit especially when a methanol plant is not nearby. However, larger refineries or ethylene plants with a reasonable quantity of byproduct C_4's and C_5's might find upgrading to oxygenates attractive.

The market for oxygenates is very promising. The refining industry took a long time to evaluate Methanol, Ethanol and MTBE as oxygenates. Everyone in the industry has accepted the disadvantages of Methanol, even when used with a co-solvent. Ethanol is too expensive except where the sale price is subsidized by one agency or the other. MTBE, however, seems to have been well accepted by virtually all refiners both in Europe and the United States.

MTBE or TAME blended gasoline (up to 15 vol%) has shown the following performances:

- increased octane number for the blend
- the volatility blending properties are similar to those of refinery light gasoline component (eg. C_5 - C_6 isomerate)
- shows no phase separation, i.e., scarcely soluble in water and completely miscible in gasoline
- stable during handling and storage (no peroxide formation)
- no difference in consumption and engine horsepower
- no vapour-lock tendency
- unchanged driveability
- no difference in evaporation losses
- no corrosion problems
- no difference in cold start and low temperature accelaration
- no icing problems
- no effects on paints and elastomers normally used in commercial vehicles
- reduced polluting emissions
- no worse toxicological effect than gasoline itself.

As a result of this acceptance, MTBE useage has had a phenomenal growth in the last eight years favoured, of course, by the following factors:

- depletion of banked lead credits (in the U.S.)
- lead phasedown
- increased use of unleaded gasoline
- a recent trend on restrictions to RVP of gasoline in order to decrease ozone concentrations.

Plant start-ups reached their peak in 1986 and 1987. While we do not envisage seeing such high levels of new plant construction, at least for the next five years, we still anticipate a considerable growth in MTBE and/or TAME useage in the next five years.

Emphasis of research in the upgrading of C_4's and C_5's should be mainly on:

- development of integrated processes or processing schemes capable of processing the C_4's and C_5's to extinction;

- coprocessing of C_4's and C_5's to MTBE, TAME and gasoline pool acceptable mixture;

- catalysts - new or modified, i.e., regenerable catalysts which will increase productivity and selectivity;

- new processing routes for the production of petrochemical intermediates from C_4's and C_5's.

POTENTIAL RESEARCH AREAS IN THE UPGRADING OF C_4'S AND C_5'S

A lot of work has been done in the development of technologies for the production of MTBE. Generally speaking, these technologies also work for TAME production with little modifications. Lessons learned during the developmental stage of these processes are going to be useful in pursuing other areas of C_4's and C_5's processing. Some of these areas where further research or further technological development is needed include:

A. Production of High Purity Butene-1

Butene-1 is used as comonomer for the production of linear low density polyethylene (LLDPE).

The MTBE process is suitable for removing isobutylene from a product stream. Once the isobutylene content has been reduced to a level of less than 500 ppm, the recovery of Butene-1 and isobutane would be a simple process of fractionation. Depending on the feed quality, a hydrogenation step would precede the etherification step in order to selectively hydrogenate butadiene and traces of acetylene to arrive at the type of Butene-1 purity level required. Although Huels A.G., IFP and Engelhard offer similar processes, there is much room for improvement.

B. High Purity Isobutene from C_4 Streams:

High purity isobutene is a feedstock in high demand for the following:

- as a comonomer for elastomers (butyl rubber, polyisobutene);

- as an intermediate for the production of a wide range of speciality chemicals (tert-butyl phenols, tert-butyl amines, etc.).

Snamprogetti was the first to realize the ease with which one can manufacture high purity isobutene through MTBE decomposition. Refinements to this process route are still possible.

C. High Purity Isoamylene from Mixed C_5's

Like the high purity isobutene process, the decomposition of TAME under tightly guided process conditions would produce high purity isoamylene.

D. Dimerization of Isobutylene

The dimerization of isobutylene would produce diisobutylene (DIB).

E. TBA Synthesis

TBA, which is used as a cosolvent to MeOH, can be produced using the same ion-exchange resin that is used for MTBE synthesis. TBA is formed through the addition of water to isobutene in the presence of an acidic catalyst. The classical process uses sulfuric acid as catalyst. Huels A.G. has a patent for this process but product purity, conversion and energy consumption are process areas where improvements are still necessary.

F. Oligomerization of n-Butenes

Once isobutylene has been separated from a C_4 mixture via MTBE production, the n-butenes and butanes are easily separable. n-Butenes could be oligomerized to C_8,C_{12} etc., olefins which could be just blended into gasoline. When separated, they are mainly dimethylhexenes and are useful starting materials for alkyl-phenols or diisononylphthalates used as PVC plasticizers.

G. Hydration of n-Butene

n-Butene hydration to secondary butyl alcohol (SBA) is a process whose development would give ample SBA which is also a co-solvent to MeOH for octane number improvement. Moreover, SBA is utilized as an intermediate for the manufacture of Methyl-Ethyl-Ketone (MEK), an important solvent in coatings, adhesives, inks and oil dewaxing applications.

H. Integrated C_4 and C_5 Processing Schemes

The goal of research in this area would be to come up with an integrated processing scheme whereby the proper and economic useage of the C_4's and C_5's would be possible. Although, the nature of the feed would have a decisive role to play on which integrated scheme will be optimal for a given plant, the overall concept could apply to different plants.

I. Catalyst

At present, macroreticular ion-exchange resins predominate the commercial scene for the production of MTBE and TAME. These polymeric catalysts, however, have low thermal stability and are prone to the occurence of a progressive desulfonation reaction. Regeneration is impossible because of an irreversible change of the chemical structure with ageing of the polymeric catalyst.

Other acidic solid catalysts such as oxides, clays or zeolites, known also as strong Broensted acids, have better thermal characteristics, but are less active or less selective to MTBE synthesis. A lot of room is left for authentic research in the catalytic field, either in the form of modification of existing ion-exchange resins or in the form of the use of other catalyst which would be as selective to MTBE/TAME synthesis as the ion-exchange resins and not have their disadvantages. The addition of some noble metals, for example, to improve heat resistance of ion exchange resins allow operations at high enough temperature without causing the reverse reaction to take place, would be an area to look into. The modification of zeolites to give higher productivity and selectivity would significantly improve C_4/C_5 production economics.